Ultraviolet Spectrophotometric Determination of Iron(III) as Chloro-complex

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In order to establish a series of methods for ultraviolet spectrophotometric determination of iron(III), especially of the method based on differential absorptiometry, we have already reported the two following methods. One of them[1] is based on measurement of absorbance at 300 mμ due to the formation of ferric sulfato-complex using sulfuric acid as reagent, but in the other[2] the absorbance was measured at an isosbestic point (271 mμ) which is attributed to the equilibrium between ferric aquo ion and ferric hydroxo ion in the dilute perchloric acid solution.

Rabinowitch and Stockmeyer[3] have analyzed the absorption spectra for the ferric perchlorate solution in the presence of various amounts of OH^-, Cl^- and Br^-, and Mc. Connell and Davidson[6] have investigated the nature of the absorption spectra due to the equilibrium between ferric and ferrous ion, but they almost never refered to the absorption in the ultraviolet region. Recently, Gamlen and Jordan[4] have investigated the nature of the iron chloro-complex in the concentrated hydrochloric acid solution by ultraviolet spectrophotometry, and concluded that the highest chloro-complex formed have the formula $FeCl_4^-$.

DeSesa and Rogers[5] reported a method of spectrophotometric determination of iron based upon measurement at 342.5 mμ in 6 M hydrochloric acid solution. A recent A. S. T. M. publication[7] recommends the use of constant boiling hydrochloric acid as reagent and measurment at 370 mμ for the determination of traces of iron in copper and copper alloys.

The present paper reports an investigation of the absorption of iron(III) in a hydrochloric acid solution, and also of a differential method of spectrophotometric determination for iron using this acid as reagent. Applying this method, the purity of iron alloys has been determined by means of differential spectrophotometry.

Apparatus and Materials. — Spectrophotometric measurements were made with a Beckman Quartz spectrophotometer Model DU with 1 cm. silica cells.

The stock solution of ferric perchlorate was prepared to the concentration of 100 p.p.m. as previously described[2]. The hydrochloric acid was purified by distillation untill it gave negative test for iron. The reagent grade perchloric acid which contains no chloride and iron ions was used.

Experimental

Absorption Spectra.—The absorption spectra of ferric perchlorate in 6 M-perchloric and 6 M-hydrochloric acid solutions are shown in Fig. 1.

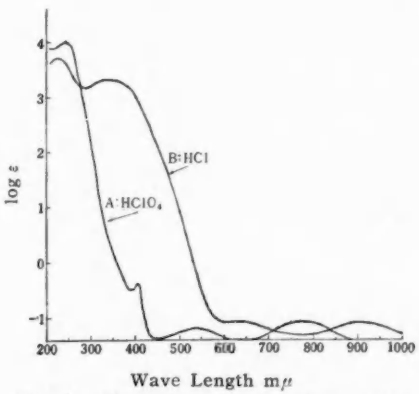

Fig. 1. Absorption Spectra of Iron(III) in 6 M Perchloric Acid and 6 M Hydrochloric Acid.

Curve A has shown good agreement with that of Rabinowitch[3], and therefore this curve may be considered as belonging exclusively to ferric aquo

1) M. Ishibashi, T. Shigematsu, Y. Yamamoto, T. Tabushi and T. Kitagawa *J. Chem. Soc. Japan (pure Chem. Sect.)* **76**, 758 (1955).
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ion. In the curve B, maxima shift to the longer region by the formation of ferric chloro-complex. As other workers have reported[3], the ordinate of curve B is the average of absorption coefficients, because the absorbing species are mixed.

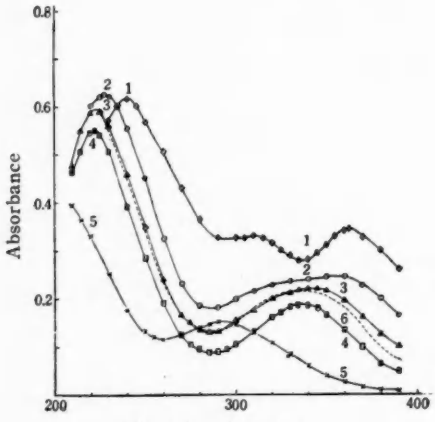


Fig. 2. Absorption Spectra of Iron(III) in the Hydrochloric Acid Solution

Fe^{3+} = ca. 4.5 p.p.m.	⊙	1	9.6 N	HCl
Temp. 12°C	⊙	2	6.4 N	〃
Ref. coresponding acid	△	3	4.8 N	〃
	⊡	4	2.4 N	〃
	×	5	—	(pH 3.4)
	·····	6	48 *f*	NaCl (pH 2.58)

The effect of change in the concentration of hydrochloric acid was then studied. Fig. 2 shows the spectra of ferric perchlorate in solution of various concentrations of hydrochloric acid. The absorption maximum of ferric aquo ion at 238 mμ shifts to the region of 320–360 mμ by adding hydrochloric acid. The position of maximum in the region of 320–360 mμ shifts to longer and the absorbance in these bands also rises, with increase in the concentration of this acid. Another band appears in the region of 220–230 mμ in the solution of hydrochloric acid, and considerable changes both in absorbance and in wave length of maxima are observed with the changes in acid concentration. Curves 5 and 6 indicate the spectra of ferric perchlorate solutions, but the former is that of extreme diluted perchloric acid solution (pH 3.4) and the latter is of the solution (pH 2.6) of 4.8 M sodium chloride. As previously reported[2], curve 5 belongs to the spectrum of the ferric hydroxo-ion $Fe(OH)^{2+}$, and thus it is considered that the hydroxo-complex has transferred to iron chloro-complex in such weak acidic medium under the considerable concentration of chloride. The similarity between curve 6 and 3 indicates that the effect of hydrogen ion concentration is little in such a concentration of chloride ion as 4.8 M.

As the formation of the ferric chloro-complexes may take place stepwise according to Bjerrum's theory of complex formation, it is necessary to investigate the effects of concentration of chloride ion under the constant acidity. Fig. 3 shows the absorption spectra in the following conditions. The concentration of iron(III) was kept constant and the constancy of the concentration of hydrogen ion could be approximately held by mixing the same molar concentration of hydrochloric and perchloric acid. The variations in the absorbance and location of the absorption bands are showed in detail as follows.

(1) 1.2 and 2.4 M H^+ (Fig. 3-1)

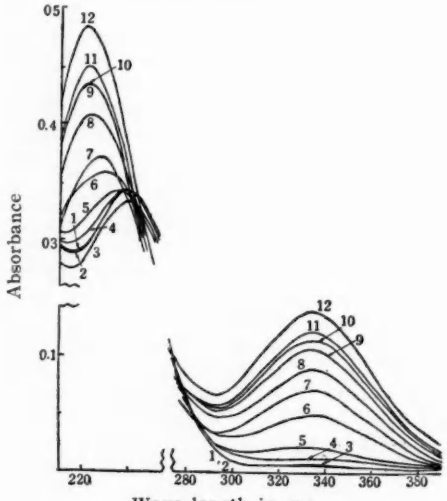


Fig. 3-1. Effect of Chloride Concn. (I) (Fe^{3+} = ca. 4.5 p.p.m, acidity = ca. 1.2 N)

	Vol. of Acid in 20 ml. HCl (ml.)	Vol. of Acid in 20 ml. $HClO_4$ (ml.)	$\lambda_{max.}$	
1	0.05	18.95	239 mμ	—
2	0.1	18.90	238	—
3	0.3	18.70	238	—
4	0.5	18.50	237	—
5	1.0	18.00	236	—
6	3.0	16.00	227	334 mμ
7	5.0	14.00	225	334_5
8	7.0	12.00	223	334
9	10.0	9.00	222	333_5
10	13.0	6.00	222_5	333_5
11	15.0	4.00	222	334_5
12	19.0	—	222	334_5

In the region of a shorter wave length, the absorption shifts to shorter, while in the longer region the maximum is kept at constant. The absorbance increases continuously with rise of the concentration of chloride ion in both bands.

(2) 4.8 M H^+ (Fig. 3-2)

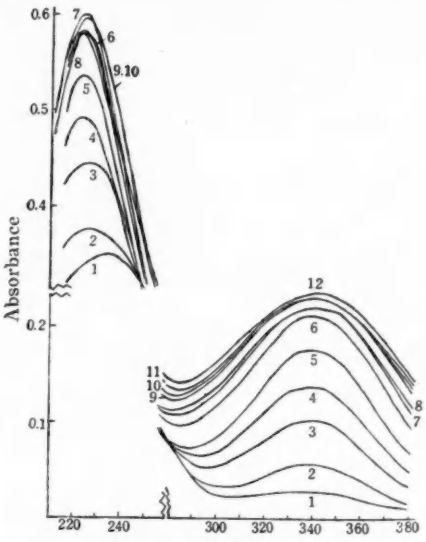


Fig. 3-2. Effected of Chloride Concentration(II) [Fe^{3+}=ca. 4.5 p.p.m. acidity =ca. 4.8 N]
The numbers on the curves are the same as in Fig. 3-1.

	λmax.	
1	234 mμ	336 mμ
2	227	334
3	224	337
4	223	338
5	222	337
6	222	340
7	221	338
8	223	341
9	223	343
10	223	343
11	222	343
12	222	343

The maximum at shorter wave length becomes shorter, that of longer wave length becomes longer, and the absorbance increases continuously in both bands.

(3) 6.4 M H^+ (Fig. 3-3)

In shorter wave length, the position of maximum is kept at constant and the absorbance rises slightly with the increase of the concentration of chloride. In the region of longer wave length, the effect of change in the concentration of chloride ion is more complicated. The position of maximum changes continuously from 342 to 354 mμ until the concentration of chloride ion grows to 1.6 M, but when the concentration becomes greater than 1.5 M, another band appears at 310 mμ. The absorbance also increases continuously while only one band is present, but when the second band appears, the change in both bands becomes very slight.

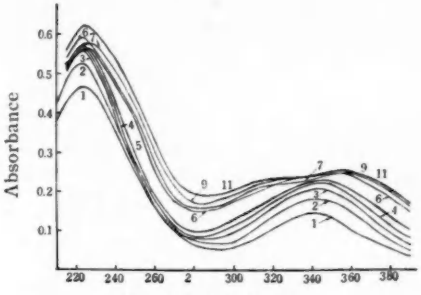


Fig. 3-3. Effect of Chloride Concn. (III) [Fe^{3+}=ca. 4.5 p.p.m. acidity=ca. 1.4 N]
The numbers on the curves are the same as in Fig. 3-1.

	λmax.	
1	223 mμ	342 mμ
2	223	343
3	223	343
4	223	343
5	223	346
6	223	351
7	224	354
9	224	354.5
11	224	355

(4) 9.6 M H^+ (Fig. 3-4)

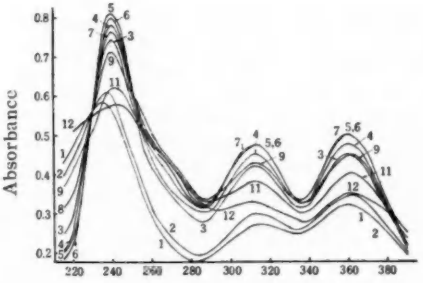
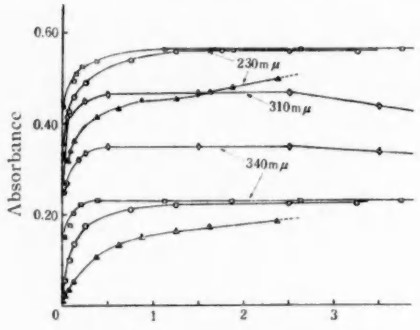


Fig. 3-4. Effect of chloride Concn. (IV) [Fe^{3+}=ca. 4.5 p.p.m. acidity=ca. 9.6 N]
The numbers on the curves are the same as in Fig. 3-1

	λmax.		
1	236 mμ	315 mμ	360 mμ
2	237	313.5	360
3	240	312	360
4	240	312	360
5	240	312	360
6	240	312	359.5
7	240.5	312	260
9	241.5	312	361
11	242	312	361
12	242	310	363

In this case remarkable changes in location and absorbance of all bands occur.

The maximum in the region of shorter wave length shifts to longer. In the region of the longer wave length, two bands exist even at the small concentration of chloride ion, and the maxima of these bands shift from 315 to 310 mμ, from 360 to 363 mμ, respectively. With increase in the concentration of chloride ion, the absorbance in all bands rises at first, and then remains constant while the chloride concentration is in the range from 0.5 to 2.4 M (Curve 5, 6 and 7), and after that it begins to diminish gradually.



Chloride Concentration in Mol.

Fig. 4. Correlation of chloride concentration and Acidity.
Acidity: △ 2.4 N, ○ 4.8 N, □ 6.4 N, ◇ 9.6 N

The complicated changes in absorption spectra are due to the stepwise formation of iron(III) chloro-complex as follows.

$$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$$
$$FeCl^{2+} + Cl^- \rightleftarrows FeCl_2^+$$
$$FeCl_2^+ + Cl^- \rightleftarrows FeCl_3$$
$$FeCl_3 + Cl^- \rightleftarrows FeCl_4^-$$

To survey the correlation of the effects of hydrogen and chloride ions, in Fig. 4 are shown the changes in absorbance at a given wave length plotted against the concentration of chloride ion at various constant acidities. From this figure, it is deduced that hydrogen ion expedites the formation of the chloro-complex when the chloride concentration is considerably low, but in the higher chloride solution, effects of acidity become small, except in the solution of 9.6 M. Since the curves in Fig. 3-4, are in accord with the spectrum of $FeCl_4^-$, calculated by Gamlen, it is found that the tetra chloro-complex is formed even at the small concentration of chloride ion when the acidity is considerably high, but it may not be formed even at higher chloride concentration if the acidity is low, as shown in Fig. 3-1, -2, and -3. The decrease in absorbance observed in Fig. 3-4, might be due to decrease of ferric ion, which may be caused by the reduction of ferric to ferrous ion in such a concentrated hydrochloric acid solution, but this assumption has not been confirmed experimentally.

Determination of Iron(III)

From the above preliminary survey it is necessary to conduct the measurement under the constant concentration of hydrochloric acid for the determination of iron (III).

Calibration curve.—The preparation of the standard iron solutions was as previously reported. A 1.002 g. of electrolytic iron (purity 99.8%) was dissolved in 4 M perchloric acid and evaporated until chloride and iron(II) became absent and then diluted to 1 l.

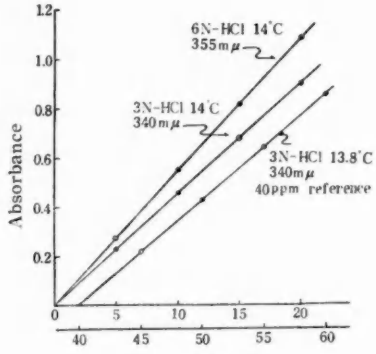


Fig. 5. Calibration Curves

First, for the ordinary absorptiometry, the calibration curve was made for the ferric solution in such concentration as 5, 10, 15 and 20 p.p.m. The concentration of the acid was held at constant in 3 M and 6 M, and the absorbance was measured at 340 and 355 mμ, respectively. In both cases Beer's law is followed in the range 0.2–20 p.p.m. of iron, as shown in Fig. 5. The sensitivity in this method is considerably low compared to the other methods; however, it is more useful by means of the differential absorptiometry. For this purpose, the solution with 40 p.p.m. of iron was used as reference, and the calibration curve was made in such concentration as 45, 50, 55 and 60 p.p.m. Results are also shown in Fig. 5 and Beer's law is followed up to 60 p.p.m. As the reference, concentration higher than 40 p.p.m. of iron is not favourable, because it reduces the sensitivity of the measurement.

Temperature.—The effects of the temperature on absorbance were investigated and the results are shown in Table I. It is seen that the effect of the temperature is almost negligible in the range 10–25°C.

TABLE I

EFFECT OF TEMPERATURE

Concn. of Iron(III): 10 p.p.m.

3 M-HCl		6 M-HCl	
Temp. C	As. at 340 mμ	Temp. C	As. at 355 mμ
9	0.440		
10	0.440	10	0.543
11	0.441	12	0.543
13	0.442	14	0.544
16	0.442	18	0.544
17	0.445	23	0.543
19	0.448	30	0.545
20	0.449		
24	0.451		
28	0.454		

TABLE II

EFFECT OF DIVERSE ION

Diverse Ion (p.p.m.)		Fe present (p.p.m.)	Fe found (p.p.m.)
Al^{3+}	200	10.0	9.9$_5$
Zn^{2+}	200	10.0	10.0$_6$
Mn^{2+}	200	10.0	10.0
Ni^{2+}	200	10.0	10.1
Co^{2+}	200	10.0	10.1
Ti^{4+}	200	10.0	10.1
Cu^{2+}	200	10.0	29.9
Cu^{+}	10	10.0	11.1

concn. of HCl;6 M, wave length: 355 mμ

Effect of diverse Ions.—Study was made on the effect of several cations. The cations were present in solution as perchlorate. Measurements were made for the solutions containing a proper amount of foreign salt with 10 p.p.m. of iron. The results are presented in Table 2. It is found that the presence of such cations as Na^{+}, K^{+}, NH_4^{+}, Co^{2+}, Zn^{2+}, Mn^{2+} and Al^{3+} do not interfere in the concentration of 200 p.p.m. As DeSesa has reported, the chloride of cations such as Cu^{2+}, Ti^{4+}, Bi^{3+} and V^{5+} in the solution of hydrochloric acid have intense absorption in the ultraviolet region, and thus their presence will interfere with the determination of iron. For Cu^{2+} and Ti^{4+}, it is found that the maximum allowable concentration was 2.0 p.p.m.

Determination of Iron in Iron-base alloy.—In order to test the reliablity of the proposed method, some iron-base alloys were shosen as samples, and the determination was done by means of differential absorptiometry.

Procedure:

A 200–150 mg of sample was dissolved in 4 M perchloric acid by warming on a sand bath. After cooling, several drops of H_2O_2 (30%) were added and then evaporated almost to dryness. The evaporation was repeated several times and the residue was dissolved in distilled water: then the solution was transferred to a 500 ml. volumetric flask and diluted to the volume. After being mixed thoroughly, an aliquot of 20 ml was pipetted into a 100 ml. volumetric flask and after 50 ml. of 6 M hydrochloric acid was added, diluted to the volume with water.

TABLE III

ANALYSIS OF IRON SAMPLES

Sample	Fe (%) Present	Found	Error (%)
J. E. S. No. 12 (low phosphor iron)	92.46	92.91	+0.4$_9$
J. E. S. No. 21 (Haematite)	61.32	61.49	+0.2$_8$
J. E. S. No. 19 (Ferrovanadium)	57.44	71.12	+27.0
J. E. S. No. 13 (Ferromanganese)	15.78	15.71	−0.4$_5$

The absorbance of the above solution was measured at 340 mμ using an iron solution (40 p.p.m.) as the reference. Results are presented in Table 3, and the error is about 0.4%. In the case of ferrovanadium alloy, the reason for the high value must be the presence of vanadium (V).

Summary

The absorption spectra have been investigated for the solution of ferric perchlorate at various concentrations of hydrochloric acid. A method for spectrophotometric determination of iron has been studied using hydrochloric acid as reagent. Effects of temperature, acidity and diverse ions have been examined and the iron content of iron-base alloys has been determined by differential method.

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Ultraviolet Spectrophotometric Determination of Iron with Ethylenediaminetetraacetic Acid

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When ethylenediaminetetraacetic acid, EDTA, is added to the solution containing a considerable amount of Fe^{3+} ion, a yellow color apparently akin to that produced by Fe^{3+}—HCl complex develops. It was already pointed out by Schwarzenbach and Heller[1] in 1951 that Fe^{3+}—EDTA complex shows an absorption in the near ultraviolet region. The absorption at about 400 mμ was also reported by Jones and Long[2] who used in their observation a solution of considerably high concentration. In 1954, Goto and Kobayashi[3] illustrated an end absorption similar to that reported by Jones and Long while Nielsch and Böltz[4] described the fact that the solution of Fe^{3+}—EDTA has an absorption maximum below 366 mμ which allows photometric estimation of the metal by EDTA. Uzumasa[5] and Nishimura[6] reported in their short communication that a dilute solution of Fe^{3+}—EDTA compound has a characteristic absorption peak at 260 mμ which is available for ultraviolet spectrophotometric determination of iron. The conditions under which the analysis is carried out have been investigated since and the results will be reported here.

Experimental

An excess of disodium salt of EDTA was added to hydrochloric acid solutions containing various amounts of iron as Fe^{3+}. Each solution was diluted to a definite volume so that the resultant concentration should be 0.1 M with respect to hydrochloric acid and 0.001 M with respect to EDTA. The absorbance of the solutions was then measured with a Beckman DU spectrophotometer equipped with 1 cm. silica cells. Distilled water was referred to as blank throughout the present observation. In Fig. 1, curve I shows the absorption spectrum of EDTA under no iron; curves II, III and IV represent the absorption spectra of Fe^{3+}—EDTA solutions which contain 5×10^{-5}, 1.5×10^{-4} and 2×10^{-4} mol. Fe^{3+}/l. respectively. The ferric ion when combined with EDTA shows, as already reported by the authors, a remarkable absorption at 260 mμ, whereas EDTA itself exhibits no absorption at this point.

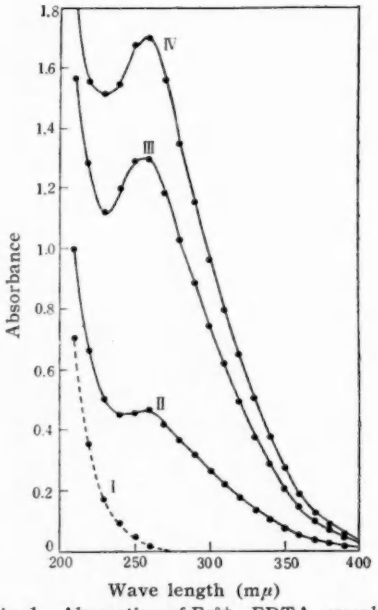

Fig. 1. Absorption of Fe^{3+}—EDTA complex.
I: without iron
II: 5×10^{-5} M Fe^{3+}
III: 1.5×10^{-4} M Fe^{3+}
IV: 2×10^{-4} M Fe^{3+}

Fig. 2 indicates the calibration curve for iron at 260 mμ obtained by the present procedure. Conformity to Beer's law was found for concentrations up to 17 p.p.m. of iron. The sensitivity[7] of the method is 0.0065 γ Fe/cm^2, a little better than that of the thiocyanate method (0.008 γ/cm^2; 480 mμ) and nearly comparable to that of the α,α'-bipyridyl method (0.007 γ/cm^2; 522 mμ)[7].

1) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).
2) S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).
3) H. Goto and J. Kobayashi, *J. Chem. Soc. Japan*, **75**, 964 (1954).
4) W. Nielsch and G. Böltz, *Mikrochim. Acta*, **1954**, 481.
5) Y. Uzumasa, *Japan Analyst*, **3**, 255 (1954).
6) Y. Uzumasa and M. Nishimura, This Bulletin, **28**, 88 (1955).
7) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed. Interscience Publishers, Inc., New York, N. Y. (1950). p. 364.

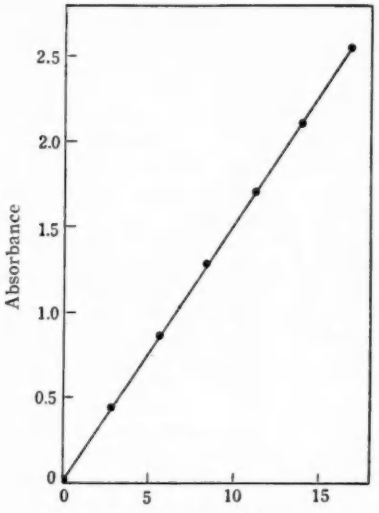

Fig. 2. Calibration curve for iron at 260 mμ.

Jones and Long[2] described in their discussion on the mechanism of the reaction that a part of Fe^{3+}–EDTA complex in the solution is converted into Fe^{2+}–EDTA complex by light, the latter returning to the former in the dark. It was also established by the present authors that the absorbance of the Fe^{3+}–EDTA solution decreases when irradiated by light while it recovers when placed in the dark (Fig. 3). The complex is stable in the dark, its absorbance remaining unchanged when even it is left for 13 hours.

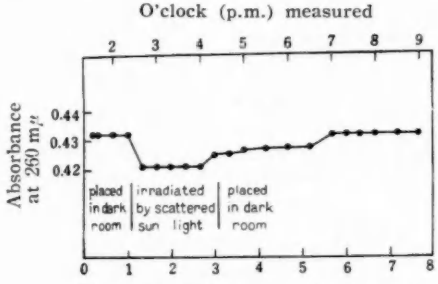

Fig. 3. Effect of light on Fe^{3+}–EDTA complex.

According to Schwarzenbach and Heller[1], the ratio Fe : EDTA in the complex is 1 : 1, which was ascertained by Jones and Long[2] after Job's continuous variation method. In the present study, a series of solutions was prepared by mixing 0.0002 M ferric iron solution and the EDTA solution of the same concentration in different ratios so that the acidity of the resultant liquid should be maintained to be constant, i. e., 0.1 M with respect to hydrochloric acid. Using these solutions, the absorbance at 260 mμ was observed, the result being in good accord with that of Jones and Long. Theoretically 1 mole EDTA is thus considered to react with 1 mole Fe^{3+} (Fig. 4). In the practical determination of iron, however, as shown in Fig. 5, EDTA might as well be used in excess, at least one and one half times as much as iron.

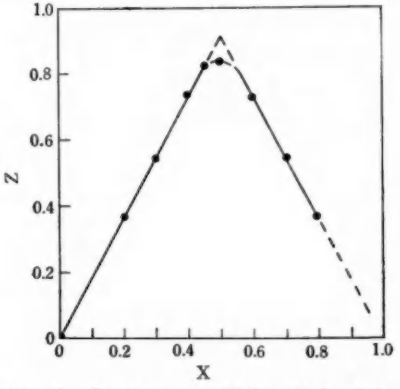

Fig. 4. Continuous variation study of the system Fe^{3+} and EDTA.
X = mol. ratio of (EDTA)/(Fe^{3+}+EDTA)
$Z = \varepsilon_2/(\varepsilon_2-\varepsilon_1)\{(As)_{obs.}-\varepsilon_1 M(1-X)\}$
Where ε_1 and ε_2 are molar extinction coeff. for Fe^{3+}–HCl and Fe^{3+}–EDTA solutions, respectively. $(As)_{obs.}$ is the absorbance observed at 260 mμ.

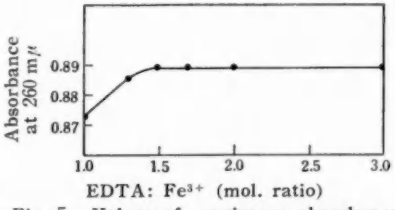

Fig. 5. Values of maximum absorbance of 1×10^{-4} M Fe^{3+} solutions at varying concentrations of EDTA.

Influence of pH.—Nielsch and Böltz[4] found the extinction of Fe^{3+}–EDTA complex depends upon the pH. This was further verified in the present investigation. By varying the amount of hydrochloric acid or sodium hydroxide to be

added, a series of solutions, each of which was 5×10^{-5} M with respect to Fe^{3+} and 1×10^{-3} M with respect to EDTA, only differing in pH values, was obtained. Their absorbance was then examined at 260 mμ. As shown in Fig. 6, Fe^{3+}-EDTA complex seems to be stable on the acid side, although its absorbance decreases rapidly below pH 0.5. In the solution containing as much as 1 M hydrochloric acid, it develops an absorption similar to that which contains no EDTA: in other words, it corresponds to the absorption of Fe^{3+}–HCl. The absorbance is also reduced on the alkaline side.

In place of hydrochloric acid, sulfuric, perchloric or acetic acid may be used since these acids have, like hydrochloric acid,

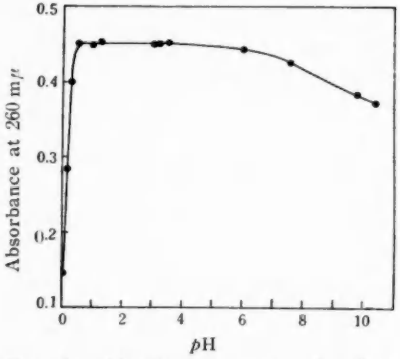

Fig. 6. Absorbance maxima for Fe^{3+}–EDTA complex. Its change with *p*H.

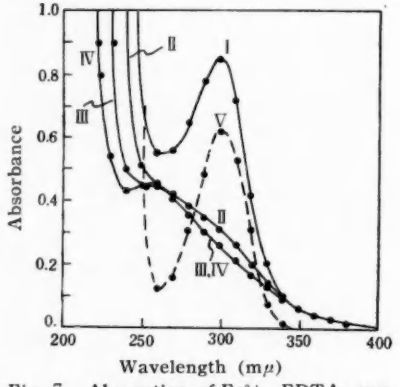

Fig. 7. Absorption of Fe^{3+}–EDTA complex (5×10^{-5} M) at varying concentrations of HNO_3.
I: in 0.1 M HNO_3
II: in 0.01 M HNO_3
III: in 0.001 M HNO_3
IV: in 0.0001 M HNO_3
V: 0.1 M HNO_3 itself

no characteristic absorption at 260 mμ. In case of nitric acid, even though it has an absorption peak at 300 mμ, its absorption is minimum at 260 mμ so that the absorbance of Fe^{3+}–EDTA in presence of nitric acid at 260 mμ remains unchanged provided that the concentration of the acid is kept lower than 0.01 M (Fig. 7).

Influence of coexisting ions.—In their study of photometric determination of iron with EDTA, Nielsch and Böltz[4] confirmed that weaker complex formers such as tartaric acid do not interfere. No observations were carried out by them on the effects of metallic ions. In order to examine the influence of the coexisting foreign substances, the absorbance measurements were carried out by the authors using the solutions with or without foreign ions. Each solution was prepared so that it was 0.1 M with respect to sulfuric or hydrochloric acid and 0.0005 M with respect to EDTA, the amount of Fe^{3+} being always kept to be 2.45 p.p.m. After each solution to which the EDTA reagent had been added was placed in the dark for 30 min., the absorbance was measured. Other conditions were kept as constant as possible throughout the measurement. The results are summarized in Table I.

Among the cations examined, alkalies and alkaline earths do not interfere. Cu^{2+}, Hg^{2+} and Ti^{4+} interfere seriously when combined with EDTA. As indicated in Fig. 8 and 9, these cations unite like Fe^{3+} with EDTA in the 0.1 M sulfuric acid solutions forming

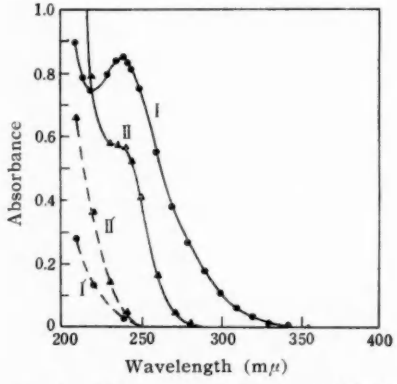

Fig. 8. Absorptions of Cu^{2+}— and Hg^{2+}— complexs in 0.1 M H_2SO_4.
I: 0.0002 M Cu^{2+} soln. with EDTA
I': 0.0002 M Cu^{2+} soln. without EDTA
II: 0.0002 M Hg^{2+} soln. with EDTA
II': 0.0002 M Hg^{2+} soln. without EDTA

TABLE I

INFLUENCE OF FOREIGN SUBSTANCES ON THE ABSORBANCE OF Fe^{3+}–EDTA COMPLEX

(2.45 p.p.m. Fe^{3+} in 0.1 M H_2SO_4 solution)

Substance added	Ion	Concentration (p.p.m.)	Absorbance at 260 mμ
None	—	0.0	0.432
NaCl	Cl^-	4,000	0.427
		10,000	0.432
NaF	F^-	20	0.431
		60	0.432
$NaNO_3$	NO_3^-	248	0.436
		620	0.442
K_2SO_4	SO_4^{2-}	1,200	0.432
		2,500	0.428
		3,700	0.432
H_3BO_3		570	0.432
		1,140	0.432
NaH_2PO_4		125	0.434
		250	0.444
$Na_2C_2O_4$		150	0.468
		300	0.495
Na-citrate		100	0.444
		200	0.435
Na-tartrate		130	0.432
		260	0.432
Li_2CO_3+HCl	Li^+	8.0	0.432
		16.0	0.432
NaCl	Na^+	2,600	0.427
		6,500	0.432
K_2SO_4	K^+	1,000	0.432
		2,000	0.428
		3,000	0.432
$MgSO_4$	Mg^{2+}	960	0.437
		4,800	0.430
$CaCO_3$+HCl	Ca^{2+}	128	0.437
		240	0.445
$MnSO_4$	Mn^{2+}	30	0.432
		70	0.434
$CuSO_4$	Cu^{2+}	0.19	0.438
		0.32	0.444
		2.0	0.613
$ZnSO_4$	Zn^{2+}	200	0.432
		400	0.437
$CdSO_4$	Cd^{2+}	1,140	0.432
$HgCl_2$	Hg^{2+}	10.3	0.456
		51.4	0.495
$SnCl_2$	Sn^{2+}	700	0.437
$CoCl_2$	Co^{2+}	6	0.433
		20	0.434
$NiSO_4$	Ni^{2+}	7	0.435
		20	0.436
		60	0.438
$Cr_2(SO_4)_3$	Cr^{3+}	10	0.433
		18	0.446
$Al_2(SO_4)_3$	Al^{3+}	100	0.427
		200	0.432
		350	0.438
$Ti(SO_4)_2$	Ti^{4+}	0.7	0.438
		20	1.004
$Ge(SO_4)_2$	Ge^{4+}	100	0.433

(2.45 p.p.m. Fe^{3+} in 0.1 M HCl solution)

None	—	0.0	0.420
$BaCl_2$	Ba^{2+}	40	0.420
		70	0.422
$SrCO_3$+HCl	Sr^{2+}	400	0.436

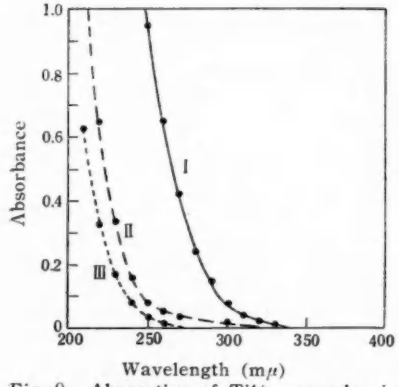

Fig. 9. Absorption of Ti^{4+}— complex in 0.1 M H_2SO_4.
I: 4×10^{-4} M Ti^{4+} soln. with EDTA
II: 4×10^{-4} M Ti^{4+} soln. without EDTA
III: EDTA only, 0.1 M H_2SO_4

complexes which exhibit remarkable absorption in the ultraviolet region. As expected from the curves in Fig. 1, 8 and 9, the effect of Cu^{2+}, Hg^{2+} or Ti^{4+} may be reduced to a certain extent if the measurement of Fe^{3+} is carried out in the range longer than 260 mμ.

Fe^{2+} can be determined by the present method if the ion is previously oxidized to Fe^{3+} by adding a dilute potassium permanganate solution in acid medium until the solution develops pink color. In this case, the absorbance changes for some time after EDTA is added. It is therefore desirable that the measurement is carried out 90 min. after the addition of the reagent.

Nitrate interferes when it exists at a certain concentration. As described above, this is certainly due to the absorption of the nitrate ion itself.

Summary

A dilute solution of Fe^{3+}–EDTA complex has a characteristic absorption peak at 260 mμ which is available for ultraviolet spectrophotometric determination of iron. An excess of disodium salt of EDTA was added to 0.1 M hydrochloric acid solution containing various amounts of iron as Fe^{3+} and the absorbance was measured with a Beckman DU spectrophotometer. A calibration curve for iron at 260 mμ was obtained and conformity to Beer's law was found for concentrations up to 17 p.p.m. of iron. The sensitivity of the method is 0.0065 γ/cm^2.

The absorbance of Fe^{3+}–EDTA solution decreases when irradiated by light, while it recovers when placed in the dark.

Fe^{3+}–EDTA complex is stable in acidic medium, although its absorbance decreases rapidly below pH 0.5. The absorbance is also reduced on the alkaline side.

Hydrochloric, sulfuric, perchloric or acetic acid can be used in the determination. Nitric acid is used only when the concentration is kept in a certain limited value, this acid having the absorption maximum at 300 mμ and the minimum at 260 mμ.

Influence of the coexisting substances on the absorption measurement of Fe^{3+}–EDTA complex was examined. Among the cations examined, alkalies and alkaline earths do not interfere. Cu^{2+}, Hg^{2+} and Ti^{4+} interfere seriously when combined with EDTA, because their EDTA complexes show remarkable absorption in the ultraviolet region, which may suggest a new ultraviolet spectrophotometric determination of the metals.

After the work reported herein had been completed, the authors were informed of the work of Hill-Cottingham[8], who reports a somewhat similar study on iron complexes of EDTA and other chelating agents.

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8) D. G. Hill-Cottingham, *Analyst*, **80**, 906 (1955).

A Simple Method of Sulfate Microdetermination

By Fujio EGAMI and Noriko TAKAHASHI

(Received November 17, 1956)

Y. Yagi and one of the present writers (Egami)[1] devised a method to determine sulfate by dichromate titration method. Their method was modified by N. Tamiya[2]. Although the method has been shown to be sufficiently accurate and successfully applied to the microdetermination of sulfate in biochemistry, the procedure is rather complicated.

The present paper deals with the simplification of the method: sulfate is precipitated as barium sulfate, and the excess of barium is precipitated as barium chromate. Finally the excess of chromate is estimated in alkaline solution with a spectrophotometer at 375 mμ. The optical density and the quantity of sulfate are in the linear relation.

1) Y. Yagi and F. Egami, *J. Chem. Soc. Japan*, **67**, 19 (1947).
2) N. Tamiya, *J. Jap. Biochem. Soc.*, **22**, 59 (1950).

Analytical Procedure

(Reagents)

a) Barium chloride, 0.01M.

b) Potassium dichromate, a little more than 0.005 M.

c) Sodium acetate, 20% (w/v).

d) Sodium hydroxide, 1 N.

(Method of Analysis)

1) Six ml. or less of the neutralized test solution (containing sulfate sulfur in the range 10–300 γ) and 1 ml. of barium chloride are placed in a 10 ml. measuring flask, and the flask is allowed to stand for about one hour. The complete precipitation of barium sulfate takes place.

2) Two ml. of sodium acetate solution is added to the flask, and the flask is kept in an ice bath for twenty minutes.

3) One ml. of potassium dichromate is then added to the flask, the reagents are

TABLE I

DETERMINATION OF SULFATE IN RAIN WATERS AND NATURAL SULFURIC ESTERS

Sample	Sample taken	Sulfur concn. found (γ)	Sulfur concn. found (%)	Total sulfur when 60γ of sulfur was added to the sample* (γ)	Recovery (%)
Potassium chondroitinsulfate	2.400mg	125	5.21	185	
		126	5.25	187	99.5
		130	5.42	186	
Potassium charoninsulfate	1.216mg	178	14.6	237	
		183	15.0	251	100.8
		186	15.3	244	
Rain water I	100ml	198	—	267	103.4
Rain water II	100ml	82	—	136	95.5

* A small quantity of sulfate added to the test solutions was always quantitatively recovered

TABLE II

DETERMINATION OF SULFATE IN SYNTHESIZED SULFURIC ESTERS

Sample	Sample taken (mg)	Sulfer concn. Calcd. (γ)	Calcd. (%)	Found. (γ)	Found. (%)	Relative error (%)
Potassium ethyl sulfate	0.672	131	19.5	125	18.6	4.62
	1.058	206		202	19.1	2.05
Potassium p-nitrophenyl sulfate	0.985	123	12.5	130	13.1	5.37
	1.244	155		166	13.3	6.66

mixed well, the volume is brought to the 10 ml. mark with distilled water and the flask is kept cold for further twenty minutes.

4) The reaction mixture is transferred into a centrifugal tube. After being centrifuged, two ml. of the clear supernatant is mixed with 1 ml. of sodium hydroxide solution in a 10 ml. graduated test tube, and diluted to the volume with distilled water.

5) Then the extinction of this solution is measured at 375 mμ with the spectrophotometer**, and sulfate is estimated by the standard curve obtained by known sulfate solutions using the same reagent solutions.

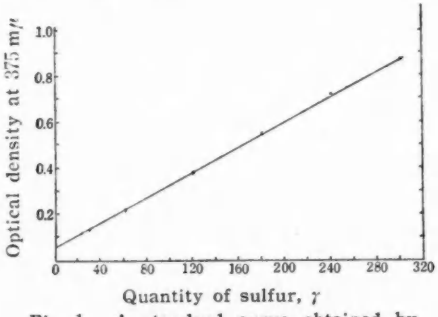

Fig. 1. A standard curve obtained by known sulfate solutions.

** We used Hitachi Type EPB-F spectrophotometer and cuvettes with a 1 cm light path.

Remarks:

1) The optical density and the quantity of sulfate are in the linear relation as shown in Fig. 1. Each time, when barium chloride or potassium dichromate solution is renewed, the standard curve must be also renewed using known sulfate solutions.

2) When a convenient spectrophotometer is not available or the test solution has an absorption band near 375 mμ, sulfate might be estimated by a spectrophotometer at a different wave length in an alkaline or an acid medium. (c.f. the absorption spectra of chromate and dichromate. Fig. 2).

3) When a large quantity of phosphate coexists with sulfate, this method can not be applied as such, unless phosphate is removed before sulfate estimation[2].

Some Examples of Analysis

This method was successfully applied to the estimation of sulfate sulfur in some natural waters, and the natural and the synthesized sulfuric esters. (Table I and Table II).

For sulfuric esters, the analytical method was slightly modified. Each sample was hydrolyzed with 0.2 ml. of concentrated hydrochloric acid under the existence of 1 ml. of barium chloride, about 3 hours on a steam bath. The hydrochloric acid was removed by evaporation and the test solution was carefully neutralyzed.

For the rain water, one ml. of barium chloride solution was added to 100 ml. of the sample solution, and the solution was carefully concentrated to a suitable volume on a sand bath.

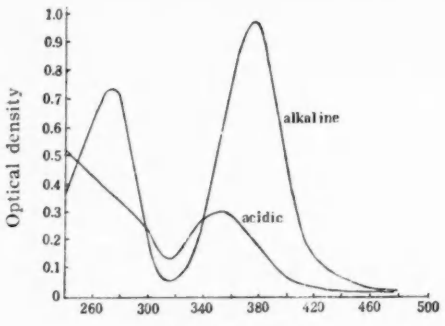

Fig. 2. The absorption spectra of chromate and dichromate (10^{-4} M).

Discussion

1) The extinction curve of the excess chromate revealed two strong absorption peaks at 273 mμ and 375 mμ in alkaline solution, and weaker one at 350 mμ in acid solution. (Fig. 2). The relationship between the amount of sulfate and the absorbance obeyed Beer's law over the range from 10γ to 320γ of sulfate sulfur. (Fig. 1).

2) Even the absorption at 375 mμ caused by the sample itself did not seriously interfere with the determination of sulfate. For example, although p-nitrophenyl sulfate (Table II) caused some absorption at 375 mμ after hydrolysis, analytical results showed it to be fairly good. In such a case, a blank without dichromate was necessary.

3) The good stability of the color of dichromate solution was also one of the advantages of this method.

Summary

1) A simple method for sulfate microdetermination was established. Sulfate is precipitated as barium sulfate; then the excess of barium is precipitated as barium chromate. Finally the excess of chromate is estimated in alkaline solution with a spectophotometer at 375 mμ.

2) This method is able to be applied to sulfate solution containing sulfate sulfur in the range 10–300γ. (30–900γ as SO_4^{2-})

3) This method was successfully applied to the estimation of inorganic sulfate such as that in rain water and organic sulfate such as chondroitinsulfate, charoninsulfate, ethyl sulfate and p-nitrophenyl sulfate.

The expense of this study was defrayed partly by a grant from Seikagaku-Kenkyusho Ltd., to which our thanks are due.

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On the Thermal Dissociation of Organic Compounds. XII. The Effects of the Substituents on the Thermal Dissociation of Substituted Phenylureas

By Shoichiro OZAKI and Tsutomu NAGOYA

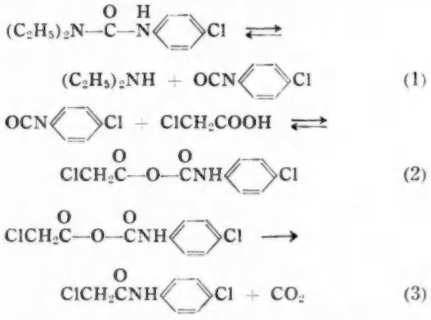
(Received August 13, 1956)

Introduction

The kinetics of the thermal dissociation of urea, di- and tri-substituted ureas in fatty acids have been studied[1-4]. In the present work, more than ten new ureas of the types, 1,1-diethyl-3-phenylureas (I), 1-pentyl-3-phenylureas (II) and 1,3-diphenylureas (III), substituted for methoxy, methyl, chloro and nitro in ortho, meta and para positions, respectively have been synthesized, and the kinetics of the thermal dissociation of these ureas in fatty acids have been studied. The effects of the substituents on the thermal dissociation of these ureas are discussed.

1) T. Hoshino, T. Mukaiyama and H. Hoshino, *J. Am. Chem. Soc.*, **74**, 3097 (1952).
2) T. Mukaiyama and T. Matsunaga, ibid., **75**, 6209 (1953).
3) T. Mukaiyama, S. Ozaki and T. Hoshino, This Bulletin, **27**, 578 (1954).
4) T. Mukaiyama, S. Ozaki and Y. Kobayashi, ibid., **29**, 51 (1956).

The dissociation of substituted ureas, e. g., 1,1-diethyl-3-(p-chlorophenyl) ureas in chloroacetic acid, takes place according to the following equations:



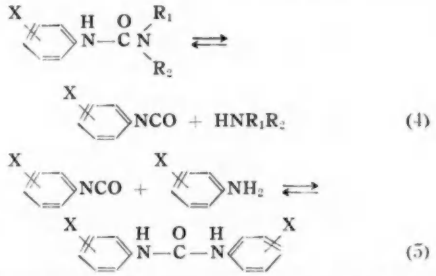
(1)

(2)

(3)

The reaction in fatty acids can be followed by measuring the rate of evolution of carbon dioxide (eq. 3), as the reaction (1) is the rate-determining step.

1,1-Diethyl-3-arylureas (I)[5] were prepared from diethylcarbamyl chloride, corresponding amines and triethylamine. 1-Pentyl-3-arylureas (II) could be obtained from pentyl isocyanate and amines. 1,3-Diarylureas (III) were obtained in the course of the syntheses of ureas (I) and (II) as mentioned below. Reactivity of aromatic amines towards isocyanate and diethylcarbamyl chloride is of a similar order to those observed by Van Opstall[6] and Linke[7] in the reaction between 1-chloro-2,4-dinitrobenzene and aromatic amines, and by C. Naegeli[8] et al. in the reaction of the amines with phenyl isocyanate. Methoxy-, methyl- and chloro- anilines react easily with pentyl isocyanate, but nitroanilines do not react at room temperature. m-Nitroaniline reacts at 80°C., and p-nitroaniline does to an extent of only 1% in 5 hours at the same temperature. The reactivity of diethylcarbamyl chloride towards amines is smaller than that of isocyanate. In the reaction of unreactive amines, such as nitro- and chloro- anilines, towards diethylcarbamyl chloride, the yields were poor, and by raising the temperature, 1,3-diarylureas were produced as byproducts. As 1,1,3-trisubstituted ureas dissociate much more easily by Eq. (4) than 1,3-diarylureas as shown in Table II and in a previous report[4], 1,3-diarylureas were obtained probably through the following mechanism.



(4)

(5)

1,3-Bis-(p-nitrophenyl)urea was produced also in the reaction of p-nitroaniline with pentyl isocyanate at 150°C.

Aniline derivatives having more than two substituents such as 2,4,5-trichloro- and 2,6-dichloro- aniline have small reactivity, and 2,4,5-trichloro- is less reactive than 2,6-dichloro-aniline.

Experimental

Ureas.—The various constants of the ureas synthesized and the experimental conditions of syntheses are summarized in Table I. As an example, the synthetic procedure for 1,1-diethyl-3-(o-methoxyphenyl)urea is given: A mixture of 4.1 g. (4/100 mole) of diethylcarbamyl chloride, 4.8 g. (4/100 mole) of o-anisidine and 5 g (5/100 mole) of triethylamine are heated under a reflux condenser with a calcium chloride tube for 2 hours at 80-90°C. The triethylamine hydrochloride precipitated is filtered off, and the salt is washed with benzene. The combined filtrate and benzene washing are washed with 2 N hydrochloric acid, and then with water. After dried over anhydrous sodium sulfate, benzene was evaporated and 5.3 g. (59%) of 1,1-diethyl-3-(o-methoxyphenyl)urea was obtained by distillation, colourless liquid boiling at 143-145°C/0.40-0.45mm.

Solvents.—The solvents were purified by the same method as described[3] previously. The boiling point of caproic acid was 104-106°C/16-17 mm. and that of chloroacetic acid was 184-185°C.

Rate measurement.—The procedure for measuring the rate of dissociation of ureas in fatty acids has been described previously[1,3]. On plotting against time the logarithm of the volume of carbon dioxide, ΔY, evolved at regular intervals of time, a straight line was obtained. This indicates a first order reaction rate. The rate constant is given by the gradient of such a plot. The molar ratio of ureas to solvents was 1 : 100 in each case.

The rate constants of the thermal dissociation of these ureas in fatty acids are summarized in Table II and in part are shown in Fig. 1 and 2.

The activation energy (Ea) of the dissociation reaction of 1,1-diethyl-3-phenylurea in chloroacetic

5) Some of ureas (I) are reported to be useful as herbicides named C. M. U. (Chlorophenyl Methyl Urea). U. S. P. 2655444, 2655445, 2655446 and 2655447. Kagaku to Kogyo (Chemistry and Chemical industry) **9**, 63 (1956).

6) Van Opstall, *Rec. trav. Chim.*, **52**, 901 (1933).

7) Linke, *Ber.*, **56**, 848 (1923).

8) C. Naegeli, A. Tyabji and C. Conrad, *Helv. Chim. Acta*, **21**, 1127 (1938).

TABLE I

UREAS AND THEIR SYNTHETIC METHODS

Ureas X—C6H4—NH—CO—N(C2H5)2	Amines X—C6H4—NH2 (g)	Diethylcarbamyl chloride (c.c.)	Solvent (c.c.)	Triethyl amine (c.c.)	Reaction temp. (°C.)	Reaction time. (hours)	M.P. (°C.)	Yield (%)	Analysis Nitrogen Calcd.	Analysis Nitrogen Found	Byproduct	M.P. (°C.)	Yield (%)	Analysis Nitrogen Calcd.	Analysis Nitrogen Found
X— H	1	1	4 benzene	0	60	0.5		0			1,3-diphenyl-urea	235	16		
〃	1	1	0	1	room temp. (5～20)	24	84.5–85	30							
〃	3.7	4.8	0	5	40	3	〃	62							
o—OCH_3	4.8	4.12	0	4.8	80	2	B.P.143–145/0.45	59	12.60	12.46					
p—OCH_3	1.4	1.5	4	1.5	room temp.	24	61.5–62	33.4	12.60	12.58					
o—CH_3	4.27	4.1	0	4.8	80–100	1	78–79	40	13.58	13.49	1,3-di-(*o*-tolyl)urea	241–242	18	11.66	11.47
m—CH_3	1	1	0	0	80–100	1		0			1,3-di-(*m*-tolyl)urea	221.5	8		
〃	1.5	1	0	2.5	room temp.	24	101–102	27.1	13.58	13.52					
p—CH_3	1	1	4	0	80	0.5		0			1,3-di-(*p*-tolyl)urea	265	25	11.66	11.89
〃	1.5	1	0	0.5	room temp.	24	67.5–68	32	13.58	13.60					
o—Cl[5]	5	4.1	0	4.8	100	2	B.P.124–126/0.4	8	Carbon 58.30 Hydrogen 6.65	58.01 6.87	1,3-di-(*o*-chlorophenyl)-urea	225–226	30	9.96	9.97
〃	2	2	0	2	room temp.	200	〃	42							
m—Cl[5]	1	1	0	1.5	〃	24	89–89.5	17	12.36	12.57					
p—Cl[5]	1	1	8	0	80	2		0			1,3-di-(*o*-chlorophenyl) urea	247	7		
〃	1	1	0	1.5	50	1	118–118.5	17							
o—NO_2	0.5	0.5	0	0.5	100	6		0							
m—NO_2	2	1.5	30	0	80	2		0							
〃	2	1.5	0	pyridine 5	100	2		0			1,3-di-(*m*-nitrophenyl)urea	244.5–245	17	18.54	18.44
〃	3	3	80	3	80	8	88–89	12			〃		11		
p—NO_2	2	2	100	2	80	120		0							
2,4,5-trichloro	1.35	1.6	0	1.5	100–120	150		0							

2,6-dichloro	1	1	0	1	room temp.	1	90.5-91.5	85					
					〃	1	120.5-121.5	83.5	11.40	11.69			
					〃	1	73	78	12.72	13.06			
					〃	1	105-105.5	82.5	12.72	12.90			
					〃	1	62.5-63	92	11.64	11.70			
					30	5	158-159	82	11.64	11.88			
					80	12	116.5-117	50	16.73	16.63			
					40	10		0					
					80	5	121-121.5	1					
					150	5		0					

X	Pentyl isocyanate												
X= H	2	2	2										
p—OCH_3	1	1	2										
m—CH_3	1	1	0										
p—CH_3	1	1	0										
m—Cl	2	1.5	2										
p—Cl	0.5	0.5	2										
m—NO_2	2	2	30										
p—NO_2	0.5	0.5	20										
〃	0.5	0.5	20										
〃	0.5	0.5	anisole 5										

acid was calculated from Fig. 2 to be Ea=22.7 Kcal.

Fig. 1. Thermal dissociation of phenylureas in chloroacetic acid: the plot of k against σ.
● 1,1-diethyl-3-phenylureas at 95°C.
△ 1-pentyl-3-phenylureas at 139.5°C.

Fig. 2. Thermal dissociation of 1,1-diethyl-3-phenylurea in chloroacetic acid: the plot of k against 1/T.

Results and Discussion

Effects of the substituents on the dissociation reaction of substituted phenylureas (I), (II) and (III) are as follow: In the 1,1-diethyl-3-arylureas (I), the value of ρ in the Hammett equation is -0.196 ± 0.028, that is, electron donating groups, such as methoxy, accelerate the reaction. The correlation coefficient r is 0.964. In the 1,3-diarylureas (III), the value of ρ is negative, and there is a large deviation from the Hammett equation in this case. Especially non-substituted diphenylurea dissociates faster than the other ureas of this type. In the 1-pentyl-3-phenylureas (II), two paths far dissociation can be considered,

TABLE II

THE RATE CONSTANTS OF THE THERMAL DISSOCIATION OF PHENYLUREAS IN FATTY ACIDS

$k \times 10^2 (min^{-1})$

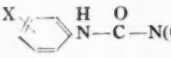
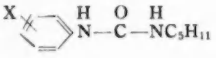
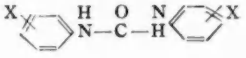
Ureas				
Fatty acids		chloroacetic acid	caproic acid	chloroacetic acid	chloroacetic acid
X	σ	at 95°C.	at 150°C	at 139.5°C	at 139.5°C
p—OCH_3	−0.268	3.55	0.81	3.83 4.69 5.13	
p—CH_3	−0.170	3.37	0.56	4.87 5.06 5.77	9.67 9.20
m—CH_3	−0.069	2.92	1.37	4.77 4.99	
H	0	2.82	1.61	5.46	10.82 10.58 10.30
p—Cl	0.227	2.77 2.70	2.92	5.47 5.75	6.72 5.61
m—Cl	0.373	2.60			
m—NO_2	0.710	2.21	2.39	7.36 6.96	5.45 4.80
	ρ	−0.196±0.028		0.1778±0.0025	
o—OCH_3		1.16			
o—CH_3		3.3			2.1
o—Cl		2.10			4.69

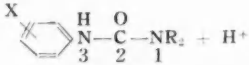
TABLE III

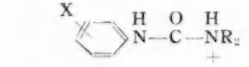
Ureas	Products	Benzyl N-phenyl-carbamate	1,3-diphenyl urea	Benzyl N-pentyl-carbamate	Dissociation ratio
(g)		(g)	(g)	(g)	(A) : (B)
4		2.2	0.1	0.1	1.59 : 1
1.5		0.5	0.28	trace	1.57 : 1

but it is impossible to determine which path is followed in the course of dissociation of the ureas in fatty acids. Therefore the dissociation ratio was determined in benzyl alcohol instead of fatty acid used in the other experiments. On heating 1-pentyl-3-phenylurea in benzyl alcohol for 4 hours at 170°C, the products shown in Table III were obtained.

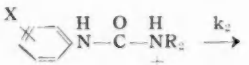
From this table the ratio A/B is equal to 1.6 for 1-pentyl-3-phenylurea at 170°C. This ratio will differ in other 1-pentyl-3-arylureas. Therefore, rate constants and ρ value (0.1778±0.025) may be insignificant in these ureas. The correlation coefficient r was low (0.895).

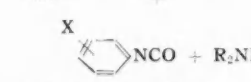
The dissociation mechanism of ureas in fatty acids is as follows[3]:





(6)





(7)

From Eqs. (6) and (7)

$$\frac{d(R-NCO)}{dt} = \frac{Kk_2(Ureas)(H^+)}{1+\frac{k_2}{k_{-1}}} \quad (8)$$

where $K = \frac{k_1}{k_{-1}}$

We can consider two cases as follows:

a) When k_{-1} is greater than k_2 or of comparable magnitude, then

$$\frac{d(R\text{—}NCO)}{dt} = CKk_2(\text{Ureas})(H) \qquad (9)$$

where C=constant

In Eq. (9), K and k_2 will fit the Hammett equation, therefore Kk_2 also will agree with it. The product $\rho\sigma$ for the reaction is given by:

$$\log \frac{Kk_2}{K_0k_{2\cdot0}} = \rho\sigma \qquad (10)$$

$$\log\frac{K}{K_0} = \rho_1\sigma$$

where $\log\frac{k_2}{k_{2\cdot0}} = \rho_2\sigma$

$$\rho = \rho_1 + \rho_2$$

Substituents having a positive σ-value decrease K (or k_1), since such substituents decrease the basicity of 1 nitrogen; and they also increase k_2, since such substituents make the deprotonation at 3 nitrogen easier. On the other hand, substituents having a negative σ-value increase K (or k_1) and decrease k_2, that is, ρ_1 will have a negative value and ρ_2 will be positive. Therefore the sign of ρ will be determined by the magnitude of ρ_1 and ρ_2, and if $|\rho_1|$ is greater than $|\rho_2|$, ρ will have a negative value, and *vice versa*.

The value of ρ obtained in this experiment was -0.198 ± 0.028 indicating that $|\rho_1|$ is greater than $|\rho_2|$. This seems improbable, since in reaction (6), the reaction center is 1-nitrogen, while in reaction (7), it is 3-nitrogen which is nearer the substituent[9]. Therefore the hypothesis (a) does not appear likely.

b) When k_2 is much greater than k_{-1}, then

$$\frac{d(R\text{—}NCO)}{dt} = k_1(\text{Ureas})(H^+) \qquad (11)$$

In this case, ρ will have a negative value from the reason just mentioned, and the experimental data are in accord with this hypothesis.

From the above, hypothesis (b) is probable rather than hypothesis (a), that is, the rate-determining step seems to be a protonation process (Eq. 6) and not a deprotonation process (Eq. 7). This contrasts with the fact[10], that in the dissociation reaction of benzyl N-arylcarbamate in a basic medium such as an amine, the dissociation rate was proportional to the rate of the deprotonation, as indicated by the positive value of ρ which was obtained.

The discussion concerning the positive ρ value in the dissociation reaction of 1-pentyl-3-arylureas (II) will not be given here for the reason mentioned in the earlier part of this result and discussion.

As to the effect of ortho substituents in 1,1-diethyl-3-arylureas, 1,1-diethyl-3-(*o*-methoxyphenyl)urea dissociates one third as fast as *p*-methoxy-, *o*-chloro- slightly slower than *p*-chloro-, and *o*-methyl- at a nearly equal rate to *p*-methyl-. With 1,3-diarylureas, *o*-methyl- dissociates a quarter as fast as p-methyl-, and *o*-chloro- at a nearly equal rate to *p*-chloro-.

The activation energy of the dissociation reaction of 1,1-diethyl-3-phenylurea in chloroacetic acid was 22.4 Kcal.; this is smaller than the value obtained with 5, 6, 7 and 11 membered polymethylene ring ureas in the same solvent (24–27 Kcal.)[11], or those of 1,3-diphenylurea in propionic acid (27.9 Kcal.) and butyric acid (28.0 Kcal.)[1]. The smaller value is due to the more facile protonation on tri-substituted ureas than on 1,3-di-substituted ureas.

Summary

Eleven new ureas of the type, 1,1-diethyl-3-arylureas and 1-pentyl-3-arylureas were synthesized. The rate constants and ρ values of thermal dissociation of these ureas in fatty acids were determined. In 1,1-diethyl-3-arylureas, the ρ value of the dissociation reaction at 95°C. in chloroacetic acid was -0.196, and it may be concluded that the protonation process seems to be the rate-determining step in the dissociation reaction of ureas in fatty acid. The activation energy was compared with those of other ureas.

The authors express their grateful thanks to Professor T. Hoshino and Mr. T. Mukaiyama for their frequent helpful advice and encouragement throughout the course of this work, and to Mr. A. Kondo for the micro analysis.

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9) T heargument is rather weak, because ρ_1 and ρ_2 are reaction constants for reactions of different types, ρ_1 referring to equilibrium (6) and ρ_2 to reaction (7).

10) T. Mukaiyama and M. Iwanami, *J. Am. Chem. Soc.*, **79**, 75 (1957).

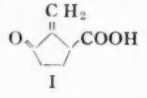
11) Unpublished data.

*Synthesis of dl-Sarkomycin (2-Methylenecyclopentanone-3-carboxylic Acid)**

By Katsuyuki TOKI

(Received December 7, 1956)

Recently, I. R. Hooper et al.[1] reported that the effective substance contained in crude sarkomycin[2] is 2-methylenecyclopentanone-3-carboxylic acid (I).



I

Though the acid is an interesting compound as an antitumor substance, nothing had been known about its synthesis when the present investigation was commenced.

The present author synthesized the acid by a four-stage process starting from ethyl cyclopentanone-3-carboxylate (II), prepared by Kay's method[3].

The Mannich reaction[4] was successfully applied to cyclopentanone-3-carboxylate to introduce a methylene group. Namely, *dl*-sarkomycin, 2-methylenecyclopentanone-3-carboxylic acid (I), was synthesized according to the scheme shown in Fig. 1.

Ethyl cyclopentanone-3-carboxylate (II) was converted into ethyl 2-(dialkylaminomethyl)-cyclopentanone-3-carboxylate hydrochloride (III) by treatment with the hydrochloride of a secondary amine (e.g. dimethylamine, diethylamine or piperidine) and formalin. Ethyl 2-methylenecyclopentanone-3-carboxylate (V) was obtained by distillation of the ethyl 2-(dialkylaminomethyl)-cyclopentanone-3-carboxylate (IV) or its hydrochloride (III) below 130°. Above 130° the substance showed a tendency to become a tarry matter. Hydrolysis of the ethyl ester (V) to the free acid, *dl*-sarkomycin, was accompanied by decomposition of the product under severe conditions while a large amount (80–90%) of the ester remained intact under mild conditions. The results of hydrolysis are summarized

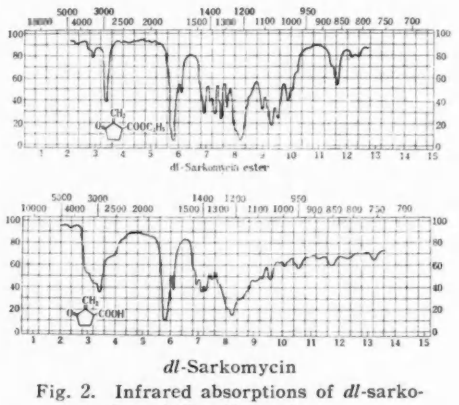


Fig. 2. Infrared absorptions of *dl*-sarkomycin and its ethyl ester.

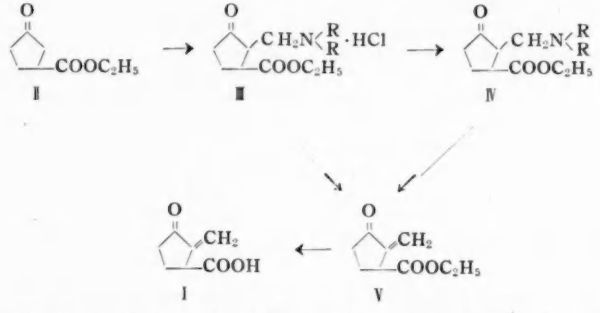


Fig. 1. Synthesis of *dl*-sarkomycin from ethyl cyclopentanone-3-carboxylate.

* Presented before the Monthly Meeting of Japan Antibiotic Research Association, at the Institute of Infectious Diseases, Tokyo, Nov. 29. (1956).

1) Hooper et al, *Antibio. & Chemo.*, **5**, 588 (1955).
2) Umezawa et al, *J. Antibio.*, Ser. A. **6**, 101, 147, 153 (1953).
3) Kay et al, *J. Chem. Soc.*, **89** 1646 (1906).
4) Mannich et al, *Arch. Pharm.*, **267**, 575 (1936).

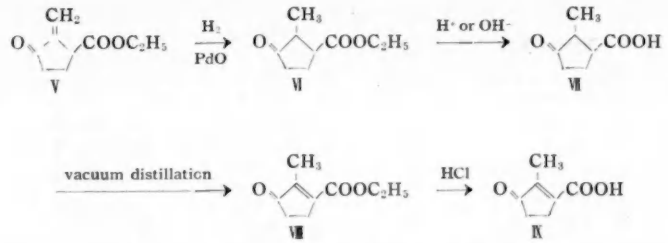


Fig. 3. Determination of the structure of V.

in Table I. Piperidine and hydroquinone had no inhibiting effect against decomposition of *dl*-sarkomycin.

The final product, *dl*-sarkomycin (I), was obtained in an oily form. The infrared spectra of the synthetic and the natural sarkomycin[1] were essentially identical and exhibited a characteristic peak at 6.1 μ (Fig. 2).

An unsuccessful attempt was made to synthesize V from IV by means of Hofmann's degradation. Treatment of the quaternary ammonium salt prepared from IV and methyl iodide or ethyl iodide with wet silver oxide or an anion exchange resin (IRA4B, IRA 400), gave no 2-methylenecyclopentanone-3-carboxylate but a tarry substance.

The present author and Hiroo Wada have also tried to prepare I by the dehydrobromination of 2-bromo-2-methylcyclopentanone-3-carboxylic acid[5], but the only product identified was 2-methyl-2-cyclopentenone-3-carboxylic acid[1,5].

Since ethyl 2-methylenecyclopentanone-3-carboxylate (V) and 2-methylenecyclopentanone-3-carboxylic acid (I) are unstable compounds, the former was transformed into stable derivatives in order to establish its structure as shown in Fig. 3.

Hydrogenation of ethyl 2-methylenecyclopentanone-3-carboxylate (V) with palladous oxide in methanolic solution followed by hydrolysis with methanolic potassium hydroxide under reflux gave a product which was identified as 2-methylcyclopentanone-3-carboxylic acid (VII) by a mixed melting point determination and a comparison of infrared absorption spectra in Nujol (in Fig. 4) with an authentic specimen prepared by Newman's[5] or Robinson's[6] procedure.

The substance (VIII) obtained by distilling the ester V under a reduced pressure was hydrolyzed with dilute hydrochloric acid to a free acid, which was identified with 2-methyl-2-cyclopentenone-3-carboxylic acid (IX) by a mixed melting point determination and a comparison of infrared spectra (Fig. 5) with an authentic specimen[1,5].

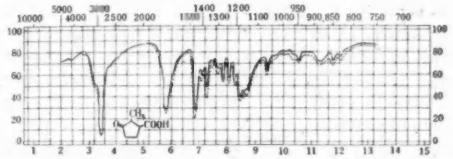


Fig. 4. Infrared absorption of 2-methylcyclopentanone-3-carboxylic acid.
····· Authentic specimen
—— Product from V

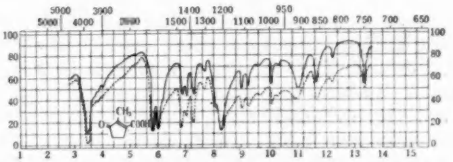


Fig. 5. Infrared absorption of 2-methyl-2-cyclopentenone-3-carboxylic acid.
····· Authentic specimen
—— Product from V

The structure of the synthetic 2-methylenecyclopentanone-3-carboxylic acid (I) was determined in the same manner (Fig. 6). Namely, 2-methylenecyclopentanone-3-carboxylic acid (I) was reduced to 2-methylcyclopentanone-3-carboxylic acid with platinum oxide in methanol at ten atmospheres, and the product was identified with the authentic specimen prepared by Newman's[5] or Robinson's[6] procedure by the melting point and the infrared absorption spectra (Fig. 5).

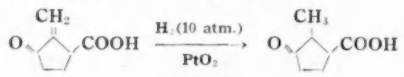


Fig. 6.

5) Newman, *J. Org. Chem.*, **19**, 1717 (1954).

6) Robinson, *J. Chem. Soc.*, **1937**, 1588.

TABLE I

No.	Hydrolysis: Concentration of HCl and Solvent	Temp. °C	hrs.	Yield of Acid	Antibacterial Activity[2]	Anti-tumor activity[3]
1	5% HCl-Acetone	21	5 1/3	5-8%	500mg.*/g	++
2	10% HCl-Acetone	21	5 1/3	10%	800-900mg.*/g	++
3	5% HCl-Acetone	35	5 1/3	7-8%	500mg.*/g	++
4	5% HCl-Acetone	21	10	12%	600-700mg.*/g	++
5	5% HCl-Acetone[1]	21	5 1/3	3-5%	800-900mg.*/g	++

1) A small amount of piperidine or hydroquinone was added. The values are the average.
2) Staphylococcus aureus 209 p.
3) Ehrlich carcinoma

While the resolution of the synthetic *dl*-sarkomycin is now under investigation, the effect of the racemic sarkomycin on the growth of Ehrlich carcinoma was tested as follows[2]: The ascites of mice bearing Ehrlich ascites carcinoma was taken seven days after the transplantation of the tumor cells and diluted with isotonic saline to prepare the cell suspension containing 2.5 million tumor cells in one ml., and 0.2 ml. of the suspension was injected intraperitoneally to mice.

dl-Sarkomycin, and Sarkomycin "Banyu HS-94" for comparison, both dissolved in isotonic saline, were intraperitoneally injected at the dosage of 2.5mg./0.2ml./mouse at an hour after the inoculation of the tumor cells and then once daily for 12 days. The results are shown in Fig. 7 and Table I. The antistaphylococcal activity (500-1000 mg.*/g.) of the synthetic sarkomycin was lower than that of the natural one[2]. On the other hand, the synthetic sarkomycin showed a greater antitumor activity in tests on Ehrlich ascites carcinoma of mice[2] and in the agar-cell plate method[7,8]. The relatively lower antibacterial potency of the synthetic products is considered partly due to decomposition and presence of *d*-isomer.

Details of the biological studies on the synthetic sarkomycin will be published elsewhere.

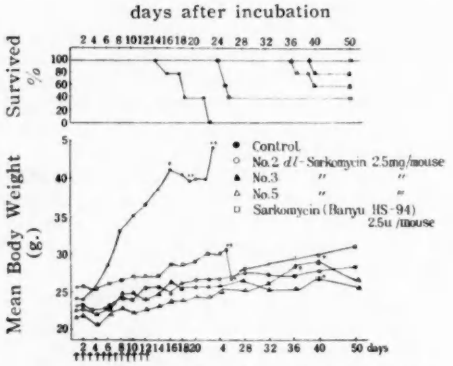


Fig. 7. The effect of synthetic Sarkomycin on Ehrlich carcinoma.

Experimental

Ethyl 2-(Piperidinomethyl)-cyclopentanone-3-carboxylate Hydrochloride (III, 2R=$(CH_2)_5$).—A mixture of 10 g. (0.06 mole) of ethyl cyclopentanone-3-carboxylate (II), 7.2 g. (0.06 mole) of piperidine hydrochloride, and 4.3g. of 37% formalin was stirred on a water bath at 75-80° for thirty minutes and then at the room temperature for additional thirty minutes. The solvent was removed under a reduced pressure. The hydrochloride, colorless needles, showed m.p. 215-220° (decomposition). (Sintering at 155-156°), when recrystallized from methyl alcohol. Yield 6.2 g. (35%).

Anal. Found: C, 57.91; H, 8.47; N, 4.91. Calcd. for $C_{14}H_{24}O_3NCl$: C, 58.13; H, 8.30; N, 4.84%.

It was considered that the residual oil separated from crystals by filteration was one of the stereoisomeride of ethyl 2-(piperidinomethyl)-cyclopentanone-3-carboxylate hydrochloride. The oil could be used for next reaction.

Ethyl 2-(Dimethylaminomethyl)-cyclopentanone-3-carboxylate (IV, R=CH_3).—A mixture of 52 g. (0.33 mole) of ethyl cyclopentanone-3-carboxylate (II), 24 g. (0.3 mole) of dimethylamine hydrochloride and 24 g. of 37% formalin was heated at 75-80° with stirring for forty minutes. After removal of solvent from the reaction mixture, a syrupy residue was obtained, and attempts to bring it to crystallization were unsuccessful. It was used without further purification.

To a solution of ethyl 2-(dimethylaminomethyl)-cyclopentanone-3-carboxylate hydrochloride in a small amount of water was added a small excess of 5% aqueous solution of sodium

7) Umezawa et al, *J. Antibio.*, Ser. A. 9, 135 (1956).
8) Yamamoto, *Gann*, in press.

carbonate with cooling. The reaction mixture was extracted with ether and the extract, after being washed with a saturated aqueous sodium chloride solution, was concentrated under a reduced pressure. 22 g. of IV was obtained.

Ethyl 2-(Diethylaminomethyl)-cyclopentanone-3-carboxylate Hydrochloride (III, R=C_2H_5).—A mixture of 4.7 g. (0.03 mole) of ethyl cyclopentanone-3-carboxylate (II), 3.3 g. of diethylamine hydrochloride, 2.3 g. of 40% formalin, and 1 ml. of methanol, was warmed on a water bath for twenty minutes and then allowed to stand for ten minutes with stirring at the room temperature. The hydrochloride obtained by removal of the solvent from the reaction mixture under a reduced pressure, was semisolid mass. Yeild 3.1g. (37%).

Anal. Found: C, 55.96; H, 8.24; N, 4.97. Calcd. for $C_{13}H_{24}O_3NCl$: C, 56.32; H. 8.66; N, 5.05%.

Ethyl 2-Methylenecyclopentanone-3-carboxylate (V).—(a) From ethyl 2-(piperidinomethyl)-cyclopentanone-3-carboxylate hydrochloride (III, 2R=$(CH_2)_5$). To a solution of 6.2 g. (0.02 mole) of ethyl 2-(piperidinomethyl)-cyclopentanone-3-carboxylate hydrochloride in a small amount of water was added a small excess of 5% aqueous sodium carbonate with cooling. The reaction mixture was extracted with ether and the extract, after being washed with a saturated aqueous solution of sodium chloride, was concentrated under a reduced pressure. 4.4 g. of oily ethyl 2-(piperidinomethyl)-cyclopentanone-3-carboxylate (IV, 2R=$(CH_2)_5$) was obtained.

Anal. Found: C, 66.19; H, 9.23. Calcd. for $C_{14}H_{23}O_3N$: C, 66.40; H, 9.09%.

Ethyl 2-(piperidinomethyl)-cyclopentanone-3-carboxylate (4.4 g.) was distilled under a reduced pressure at 90–102°/0.5 mm. and 1.6 g. of pure ethyl 2-methylenecyclopentanone-3-carboxylate (V) was obtained.

Anal. Found: C, 64.11; H, 7.25. Calcd. for $C_9H_{12}O_3$: C, 64.29; H, 7.14%.

The 2,4-dinitrophenylhydrazone of ethyl 2-methylenecyclopentanone-3-carboxylate melted at 176–177°C.

Anal. Found: C, 51.53; H, 4.61; N, 16.15. Calcd. for $C_{15}H_{16}O_6N_4$: C, 51.72; H, 4.60; N, 16.09%.

(b) From ethyl 2-(dimethylaminomethyl)-cyclopentanone-3-carboxylate (IV, R=CH_3). Ethyl 2-(dimethylaminomethyl)-cyclopentanone-3-carboxylate (22 g.) was distilled under a reduced pressure. Ethyl 2-methylenecyclopentanone-3-carboxylate (V) (6.2 g.)distilled at 80–105/0.3mm.

Anal. Found: C, 64.25; H, 7.11. Calcd. for $C_9H_{12}O_3$: C, 64.29; H, 7.14%.

The 2,4-dinitrophenylhydrazone melted at 176–177°.

(c) From ethyl 2-(diethylaminomethyl)-cyclopentanone-3-carboxylate hydrochloride (III, R=C_2H_5). Ethyl 2-(diethylaminomethyl)-cyclopentanone-3-carboxylate hydrochloride (4.1 g.) was heated at 130–140° and then distilled under a reduced pressure. Ethyl 2-methylenecyclopentanone-3-carboxylate (V) (0.2 g.) distilled at 95–104°C/0.5 mm.

Anal. Found: C, 64.27; H, 7.21. Calcd. for $C_9H_{12}O_3$: C, 64.29; H, 7.14%.

The 2,4-dinitrophenylhydrazone melted at 176–177°C.

Anal. Found: C, 51.68; H, 4.48; N, 16.03. Calcd. for $C_{15}H_{16}O_6N_4$: C, 51.72; H, 4.60; N, 16.09%.

2-Methylenecyclopentanone-3-carboxylic Acid (I).—A mixture of 5.0 g. (0.03 mole) of ethyl 2-methylenecyclopentanone-3-carboxylate (V) and 50 ml. of 5% HCl-acetone was allowed to stand at 21° for ten hours and then an excess of aqueous sodium carbonate was added to the mixture with cooling. After removal of acetone under a reduced pressure, the reaction mixture was shaken with ethyl acetate repeatedly. The ethyl acetate layer was washed with 5% aqueous sodium carbonate. The combined aqueous solution was then acidified with diluted hydrochloric acid with cooling, saturated with ammonium sulfate and extracted with ether. The ether solution was concentrated under a reduced pressure. A pale yellow oil was obtained in a yield of 0.6 g, (14%), and gave a marked inhibiting effect on the growth of Ehrlich ascites carcinoma.

Anal. Found: C, 59.51; H, 5.29. Calcd. for $C_7H_8O_3$: C, 60.00; H, 5.71%.

The recovered ester (V) amounted to 3.8 g.

Ethyl 2-methylcyclopentanone-3-carboxylate (VI).—A solution of 1.35 g. of ethyl 2-methylenecyclopentanone-3-carboxylate (V) in 10 ml. of methanol was reduced with equimolecular hydrogen in the presence of palladous oxide. After removal of the solvent, the residual oil was distilled at 110–112°/28 mm. Yield 1.30 g. n_D^{23} 1.4595.

The 2,4-dinitrophenylhydrazone of ethyl 2-methylcyclopentanone-3-carboxylate, when recrystallized from methanol, melted at 162–163°.

Anal. Found: C, 51.05; H. 5.18; N, 16.12. Calcd. for $C_{15}H_{18}O_6N_4$: C, 51.43; H, 5.14; N, 16.00%.

2-Methylcyclopentanone-3-carboxylic Acid (VII).—A mixture of 0.8 g. of ethyl 2-methylcyclopentanone-3-carboxylate (VI), 0.8 g. of sodium hydroxide, and 10 ml. of methanol, was heated on a water bath under reflux. After removal of methanol, the residue was poured into water and the whole mixture was extracted with ether. After removal of the solvent, the residue was allowed to stand in a refrigerator over night. The colorless plates, recrystallized from ether-petroleum ether (1 : 1), melted at 90–91°C. A mixture of the product with the authentic 2-methylcyclopentanone-3-carboxylic acid melted at 90–91°C.

Anal. Found: C, 58.89; H, 7.34. Calcd. for $C_7H_{10}O_3$: C, 59.15; H, 7.04%.

The 2,4-dinitrophenylhydrazone melted at 162–163°C.

2-Methylcyclopentanone-3-carboxylic Acid from 2-Methylenecyclopentanone-3-carboxylic Acid (I).—2-Methylenecyclopentanone-3-carboxylic acid (0.1 g.) in methanol solution,

with addition of 0.01 g. of platinum oxide, was reduced with hydrogen in an autoclave at 10 atm. at room temperature. On removal of the catalyst by filtration and of the solvent by evaporation under a reduced pressure, colorless crystals were obtained m.p. 90–91°C.

Anal. Found: C, 58.78; H, 7.00. Calcd. for $C_7H_{10}O_3$: C, 59.15; H, 7.04%.

The 2,4-dinitrophenylhydrazone melted at 162–163°C.

Ethyl 2-Methyl-2-cyclopentenone-3-carboxylate (VIII).—When ethyl 2-methylenecyclopentanone-3-carboxylate (V) was distilled at 80–92°/0.5 mm, ethyl 2-methyl-2-cyclopentenone-3-carboxylate (VIII) was obtained. n_D^{31} 1.4852.

The 2,4-dinitrophenylhydrazone, recrystallized from ethanol, melted at 176°C with decomposition.

Anal. Found: C, 51.59; H, 4.29; N, 16.31. Calcd. for $C_{13}H_{16}O_6N_4$: C, 51.72; H, 4.60; N, 16.09%.

2-Methyl-2-cyclopentenone-3-carboxylic Acid (IX).—(a) Ethyl 2-methyl-2-cyclopentenone-3-carboxylate (VIII) (0.5 g.) was refluxed with 10 ml. of 5% methanolic potash on a water bath for two hours. Colorless crystals thus obtained had m.p. 175° (from benzene), and weighed 0.4g.

Anal. Found: C, 59.63; H, 5.31. Calcd. for $C_7H_8O_3$: C, 60.00; H, 5.71%.

The 2,4-dinitrophenylhydrazone, recrystallized from ethanol, melted at 260°C with decomposition.

Anal. Found: C, 48.70; H, 3.62; N, 17.41. Calcd. for $C_{13}H_{12}O_6N_4$: C, 48.75; H, 3.75; N, 17.50%.

(b) A mixture of 1 g. of ethyl 2-methyl-2-cyclopentenone-3-carboxylate (VIII) and 10 ml. of 5% HCl-acetone solution was allowed to stand at 21° for five hours. Recrystallization from benzene gave colorless crystals melting at 175°. Yield 0.5 g.

Anal. Found; C, 59.89; H, 5.69. Calcd. for $C_7H_8O_3$: C, 60.00; H, 5.71%.

The 2,4-dinitrophenylhydrazone, recrystallized from ethanol, melted at 260° with decomposition.

Anal. Found: C, 49.01; H, 3.82; N, 17.22. Calcd. for $C_{13}H_{12}O_6N_4$: C, 48.75; H, 3.75; N, 17.50%.

Summary

dl-Sarkomycin (2-methylenecyclopentanone-3-carboxylic acid) was synthesized in a four-stage process starting from ethyl cyclopentanone-3-carboxylate, prepared by Kay's procedure. Namely, ethyl cyclopentanone-3-carboxylate was converted into ethyl 2-(dialkylaminomethyl)-cyclopentanone-3-carboxylate and thence to ethyl 2-methylenecyclopentanone-3-carboxylate. The ester was hydrolyzed to 2-methylenecyclopentanone-3-carboxylic acid with diluted hydrochloric acid. The final product was a pale yellow oil and was effective in inhibiting the growth of Ehrlich carcinoma of mice.

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Untersuchungen über die photochemischen Additionsreaktionen. IV. Die Anlagerungen von Thioessigsäure an Propargylalkohol und einige Propargylester

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Im Rahmen unserer Uutersuchungen über die photochemischen Additionsreaktionen[1] haben wir festgestellt, dass bei den Anlagerungsreaktionen von Thioessigsäure an propargylalkohol, Propargylacetat und Propargylborat sich eine sehr befriedigende Ausbeute an Monoaddukten und Diadduкten der Thioessigsäure ergibt. Aus Monoaddukten und Diaddukten erhielten wir so eine gute Ausbeute an Derivat des 2-Oxypropylaldehyds bzw. an 2,3-Dithiopropanol.

Die Additionen von Thioessigsäure an Acetylenkohlenwasserstoffe sind von Bader, Cross, Heilbron und Jones[2] eingehend untersucht worden. Sie haben gefunden, dass die Addition von Thiosäure an monosubstituierte Acetylene "anormal" verläuft, entgegen der Regel von Markownikow. Als Vertreter der monosubstituierten Acetylene wurden von diesen englischen Forschern Hexin-1, Octadiin-1,7, Phenyl-, *p*-Methoxy-phenyl-acetylen auf ihre Reaktionsweise gegenüber Thiosäure hin zumeist unter Anwendung von peroxydischen Katalysatoren wie Benzoylperoxyd, Ascaridol[3] oder mit Hilfe von ultraviolettem Licht bearbeitet und zu Mono- oder Diaddukten übergeleitet. Nahezu gleichzeitig versuchte Behringer[4] unter anderer Zielsetzung dieselben Anlagerungen mit denselben Verbindungen. Es war beabsichtigt, durch Anlagerung eines Mols Thiosäure an Acetylen oder monosubstituierte Acetylene an S-Vinyl-thiosäure-ester und durch deren Polymerisation—analog der des Vinylacetats—an einfache oder substituierte Polyvinyl-thiosäure-ester zu gelangen. Aber das wurde nur unvollständig erreicht. Gegenüber den Reaktionsbedingungen bei Jones et al. arbeitete Behringer nur mit Erhitzung der zwei Komponenten in Anwesenheit von Kaliumthioacetat oder in Abwesenheit von Katalysatoren, und erhielt dieselben Resultate wie bei Jones et al. Auch Versuche über Anlagerung von Thiosäure an Äthinylcarbinole unter den gleichen Bedingungen wie bei Jones et al. wurden 1956 von Bader[5] mitgeteilt. Bei seinen Versuchen über Äthinylcarbinole erwies sich die Anwendung von Benzoylperoxyd, welches bisher bei Anlargerung von Thiosäure an ungesättigte Verbindungen als Katalysator benutzt worden war, als unwirksam.

Durch die Ergebnisse dieser Arbeiten ist klargestellt, dass die Anlagerungen von Thiosäure besonders an Äthinylcarbinole und an die niederen Glieder der Acetylenkohlenwasserstoffe nur sehr schlechte Ausbeute ergeben.

Nach zahlreichen Anlagerungsversuchen von Thiosäure an Propargylacetat haben wir gefunden, dass die Belichtung mit ultravioletten Strahlen nach Zusatz von Azoverbindungen wie Azo-bis-isobuttersäurenitril, Azo-bis-cyclohexancarbonsäurenitril sich als beschleunigend erweist. Die 24-stündige Belichtung, mit einer 200-Watt-Quecksilberlampe[1], einer Mischung von Propargylacetat und Thiosäüre im 1 : 2 Molverhältnis in Anwesenheit von Azo-bis-isobuttersäurenitril ergab Diaddukt und Monoaddukt in einer Ausbeute von 65% bzw. 10% d. Theorie.

$$CH_2(OR)\cdot C : CH \xrightarrow{HSAc} CH_2(OR)\cdot CH : CH(SAc) + CH_2(OR)\cdot CH(SAc)\cdot CH_2(SAc) \qquad (II)$$

Bei der Untersuchung des Cyclohexenylthioacetats entdeckte Sen[6], dass, durch Einwirkung von Phenylhydrazin, für die $\cdot S\cdot CO\cdot CH_3$—Gruppe in Nachbarstellung zur Kohlenstoffdoppelbindung schliesslich die $\cdot NH\cdot NH\cdot C_6H_5$—Gruppe substituiert

1) Yamagishi, Tanaka und Hosino, dieses Bulletin, **29**, 447 (1956).
2) *J. Chem., Soc.*, **1949**, 619.
3) Cunneen, ibid., **1947**, 36; **1947**, 134.
4) *Ann.*, **564**, 219 (1949).
5) *J. Chem. Soc.*, **1956**, 116.
6) *J. Indian Chem. Soc.*, **13**, 268 (1936).

wird und sich Phenylhydrazon des Cyclohexanons ergibt. Durch die Behandlung unseres Monoaddukts mit phenylhydrazin erhielten wir phenylhydrazon des 2-Oxypropylaldehyds anstatt Phenylhydrazon des 2-Acetoxypropylaldehyds. Damit ist festgestellt, dass das Monoaddukt eine gemäss einem „anormalen" Reaktionsverlauf zu erwartende Struktur $CH_2(OR)\cdot CH:CH(SAc)$ hat. Die folgende Formel wird diesen Reaktionsverlauf zeigen.

$$CH_2(OAc)\cdot CH:CH(SAc)$$
$$[I]$$
$$+2NH_2\cdot NH\cdot C_6H_5 \longrightarrow$$
$$[CH_2(OH)\cdot CH:CH(SH)]$$
$$+2Ac\cdot NH\cdot NH\cdot C_6H_5$$
$$[CH_2(OH)\cdot CH_2\cdot CH:S]$$
$$+NH_2NH\cdot C_6H_5 \longrightarrow$$
$$CH_2(OH)\cdot CH_2\cdot CH:N\cdot NH\cdot C_6H_5+H_2S$$

Das durch Anlagerung von zwei Molekülen Thiosäuren entstehende Diaddukt erwies sich als identisch mit dem authentischen Produkt 2,3-Diacetylthio-propylacetat, das von Sjöberg[7] aus α, β-Dibromhydrinacetat und Kaliumthioacetat hergestellt wurde. Eine Bestätigung der Konstitutionen der zwei Addukten sahen wir auch in den ultravioletten Absorptionsspektren. Der Ort des Absorptionsmaximums des Monoaddukts, welches ein Chromophor $\cdot CH:CH\cdot S\cdot CO\cdot CH_3$[8] hat, ist nm 20 m$\mu$

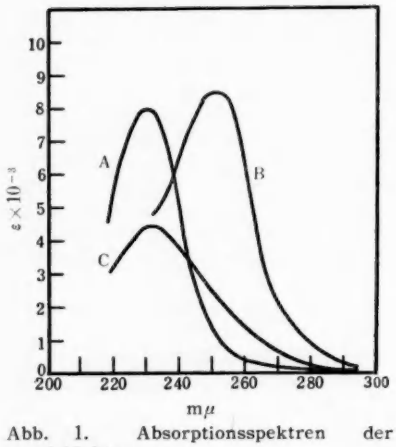

Abb. 1. Absorptionsspektren der Addukten
A: 2,3-Diacetylthio-propylacatat (II)
B: 3-Acetoxyprop-1-enylthioacetat (I)
C: Äthylthio-3-acetoxythio-propylacetat

7) *Ber.*, **75**, 13 (1942).
8) Bowden, Braude und Jones, *J. Chem. Soc.*, **1946**, 948.

weiter fort als der des Diaddukts verschoben:

2,3-Diacetylthio-propylacetat (II):

λ_{max}230mμ, ε_{max}7980,

3-Acetoxyprop-1-enylthioacetat (I):

λ_{max}250mμ, ε_{max}8500.

Das Monoaddukt polymerisiert sich, wenn man es längere Zeit in der Luft stehen lässt, allmählich zu einem braun gefärbten Harz, das elastisch ist, aber doch unter Biegekraft leicht zerbricht.

Liess man überschüssige Thiosäure auf das Monoaddukt 3-Acetoxyprop-1-enyl-thioacetat reagieren, so wurden nur 31% Ausbeute an Diaddukt isoliert. Bei Anwendung von Äthylmercaptan statt Thiosäure, das sehr glatt zu olefinischem Kohlenwasserstoff addiert[9], erhielt man eine Ausbeute von 37% an einem Addukt 2-Äthylthio-3-acetoxythio-propylacetat. Das Addukt hat ein Absorptionsmaximum an demselben Ort wie 2,3-Diacetylthiopropylacetat.

Behandelt man das Diaddukt mit 1 proz. salzsaurem Methanol und dann mit 1-N Natronlauge, so erhält man 64 proz. Ausbeute an 2,3-Dithiopropanol. 2,3-Dithiopropanol[10] ist ein wirksames Gegengift gegen Lewisit und gegen verschiedene Metallionen wie Arsen, Quecksilber, Cadmium, Gold u.a.. Im Handel führt es die Bezeichnung "BAL" (Britisch Anti-Lewisit). Andrerseits fanden wir, dass sich das Diaddukt mit Phenylhydrazin durch Erhitzung in Alkohollösung leicht in 2,3-Dithiopropanol überführen lässt, in einer Ausbeute von 75%.

$$CH_2(OAc)\cdot CH(SAc)\cdot CH_2(SAc)$$
$$+3NH_2\cdot NH\cdot C_6H_5 \longrightarrow$$
$$CH_2(OH)\cdot CH(SH)\cdot CH_2(SH)$$
$$+3Ac\cdot NH\cdot NH\cdot C_6H_5$$

Bei der Anlagerungsreaktion von Thiosäure auf propargylalkohol ergaben sich 64% Diaddukt 2,3-Diacetylthio-propanol bzw. 12% Monoaddukt, 3-Oxyprop-1-enylthioacetat. Nach Hydrolyse des Diaddukts liess sich 2,3-Dithiopropanol mit Ausbeute von 67% erhalten. Das Monoaddukt wurde durch Behandeln mit Phenylhydrazin in Phenylhydrazon des 2-Oxypropylaldehyds übergeführt.

9) Ipatieff und Friedmann. *J. Am. Chem. Soc.*, **61**, 71 (1939); Hoshino, Yamagishi und Ichikawa. *J. Chem. Soc. Japan*, **74**, 510 (1953).
10) Waters und Stocken, *Science*, **102**, 601 (1945); Stocken und Thompson, *Biochem. J.*, **40**, 535 (1946); Stocken, *J. Chem. Soc.*, **1947**, 592.

TAFEL I

Katalysator	Temp.		Zeit in Std.	Ausbeute in %	
				Monoaddukt	Diaddukt
ABC*	Raumtemp.	UV-Licht	24	9	64
ABI*	Raumtemp.	UV-Licht	48	9	64
ABI	60°	/	24	13	50
ABI	Raumtemp.	UV-Licht	6	46	20
Piperidin (0.1 g)	60°	/	24	16	13
Quecksilberacetate (0.1 g)	Raumtemp.	UV-Licht	24	5	37
Keine	60°	/	24	16	5
Keine	100°	/	24	20	5
Keine	Raumtemp.	UV-Licht	24	4	37

* ABC bedeutet: Azo-bis-cyclohexancarbonsäurenitril und ABI auf Azo-bis-isobuttersäurenitril.

Es ergab sich ferner: Bei der Anlagerung von Thiosäure an propargylborat erhielten wir ausschliesslich Monoaddukt. Dieses liess sich durch Behandln mit Wasser zu 3-Oxyprop-1-enylthioacetat verseifen, in einer Ausbeute von 61% der Theorie auf Grund von dem verwendeten Propargylborat.

Die in dieser Mitteilung beschriebenen Produkte ausser 2,3-Diacetylthio-propylacetat, 2,3-Diteiopropanol und 2-Oxypropylaldehyd[11] sind alle neue Verbindungen.

Beschreibung der Versuche

Ultraviolette Absorptionsspektren wurden in Methanol-Lösungen bestimmt.

Thioessigsäure[12].—Thiosäure wurde aus Essigsäureanhydrid und Schwefelwasserstoff dargestellt und vor dem Gebrauch frisch destilliert. Sdp. 86–88° (760 mm), 29° (68 mm).

Propargylacetat[13].—Es wurde durch Acetylierung von Propargylalkohol mittels Essigsäureanhydrid oder Acetylchlorid dargestellt. Sdp. 122–123°.

Propargylborat.—Eine Mischung von 56 g Propargylalkohol, 22.7 g Borsäure und 200 ccm Benzol wurde in einem 500 ccm-Kolben mit einem Wasserfänger unter Rückfluss erhitzt, bis kein Entstehen von Wasser im Wasserfänger mehr zu erkennen war (3 stunden). Nach dem Entfernen des Benzols wurde der Rückstand im Vakuum destilliert. Sdp. 79–81° (4 mm). Ausbeute 54.3 g (71%). Rektifizierung, Sdp. 68–69° (2 mm), n_D^{15} 1.4564.

Anal. Gef.: B, 6.20. Ber. für $C_9H_9O_3B$: B, 6.15%.

Photochemische Anlagerung von Thioessigsäure an Propargylacetat.—Die meisten der hier mitgeteilten photochemischen Anlagerungsreaktionen wurden auf folgende Weise herbeigeführt: Eine Mischung von 7.4 g (0.075 Mol) Propargylacetat, 11.4 g (0.15 Mol) Thiosäure und 0.1 g Azo-bis-isobuttersäurenitril wurde in einem zugeschmolzenen Reaktionsrohre von 80 ccm Inhalt 24 Stunden lang ultravioletter Belichtung mittels einer Quecksilberlampe von 200 Watt[1] ausgesetzt und anschliessend im Vakuum destilliert. Nach einem vorlauf unverbrauchter Materialien erhielt man 1.5 g Monoaddukt (10%) vom Sdp. 93–98° (2 mm) und 12.0 g Diaddukt (65%) vom Sdp. 130–135° (2 mm).

(a) Monoaddukt, 3-acetoxyprop-1-enylthioacetat.—Sdp. 95–97° (3 mm), n_D^{15} 1.5115.

Anal. Gef.: C, 47.86; H, 5.88; S, 19.38. Ber. für $C_7H_{10}O_3S$: C, 48.27; H, 5.79; S, 19.37% (Absorptionsspektrum: siehe Abb. 1).

Die Substanz ist ein schwach gelbes Öl von eigenartig scharfem Geruch, färbt sich an der Luft rot-braun und polymerisiert sich allmählich zu einem elastischen Harz.

(b) Diaddukt, 2,3-Diacetylthio-propylacetat.—Sdp. 92–95° (10^{-2}mm), n_D^{13} 1.5181.

Anal. Gef.: C, 43.01; H, 5.71; S, 25.16. Ber. für $C_9H_{14}O_4S_2$: C, 43.20; H, 5.64; S, 25.58%. Die Substanz ist identisch mit dem authentischen Produkt α,β,γ-Triacetyl-α,β-dithioglycerin, das von Sjöberg[7] aus Dibromhydrinacetat und Kaliumthioacetat dargestellt wurde (Absorptionsspektrum: siehe Abb. 1).

In Tafel I sind die unter verschiedenen anderen Bedingungen ausgeführten Versuche der Anlagerung von Thiosäure an Propargylacetat verzeichnet. Das Mol-Verhältnis der zwei Materialien ist 0.15 Mol : 0.075 Mol. Die Ausbeute wurde auf Grund der verwendeten Propargylacetats berechnet.

2,3-Dithiopropanol aus Diaddukt (II, R = Ac).—10 g Diaddukt wurden in 50 ccm 1proz. salzsaurem Methanol gelöst und 6 stunden lang auf 60° erhitzt. Das nach dem Entfernen des Methanols zurückgebliebene Produkt wurde mit 20 cc 1-N Natronlauge zwei Std. lang um geschüttelt. Aus der alkalischen Wasserschicht wurde der unverbrauchte Teil mit Äther entfernt und nach dem Ansäuern das 2,3-Dithiopropanol mit Äther aufgenommen. Die Ätherlösung wurde

11) *Ann.*, **335**, 219 (1904).
12) "Org. Syntheses," Vol. 31, John Wiley and Sons, Inc., New York (1951), p. 105; Clarke und Hartman, *J. Am. Chem. Soc.*, **46**, 1731 (1924).
13) U. S. Patent, 2, 340, 701 (1944); *C. A.*, **38**, 4269 (1944).

mit Magnesiumsulfat getrocknet und destilliert.

Nach einem sehr geringen Vorlauf erhielt man 3.2 g eines schwach gelben Öles von Sdp. 85–90° (1 mm).

Anal. Gef.: S, 51.45. Ber für $C_3H_5OS_2$: S, 51.64%.

Die Substanz ist identisch mit dem aus Dibromallylalkohol und prim. Natriumsulfid dargestellten 2,3-Dithiopropanol, "BAL[10]".

2,3-Dithiopropanol aus Diaddukt (II, R=Ac) und Phenylhydrazin.—2.5 g Diaddukt und 3.5 g Phenylhydrazin wurden mit 20 ccm Alkohol 6 stunden lang erhitzt und dann das Lösungsmittel abdestilliert. Das gebliebene Reaktionsgemisch wurde mit Petroläther (35–70°) extrahiert. Nach dem Entfernen des Petroläthers erhielt man 1.2 g 2,3-Dithiopropanol von Sdp. 85–90° (1 mm).

Anal. Gef.: S, 51.40. Ber. für $C_3H_5OS_2$: S, 51.64%.

Der beim Extrahieren mit Petroläther zurückgebliebene Rückstand wurde aus Alkohol umkistallisiert. Wir erhielten 4g β-Acetylphenylhydrazin in farblosen Kristallen von Schmp. 128°. Der Mischschmelzpunkt mit dem authentischen Produkt[14] aus Phenylhydazin und überschüssigem Eisessig zeigte keine Depression.

Überführung von 3-Acetoxyprop-1-enylthioacetat in Phenylhydrazon des 2-Oxypropylaldehyds.—1.7 g 3-Acetoxyprop-1-enylacetat und 3.5 g phenylhydrazin wurden mit 10 ccm Alkohol 24 Stunden lang erhitzt und dann das Lösungsmittel abdestilliert. Der Rückstand wurde mit Äthers extrahiert. Nach dem Entfernen des Äthers wurde das Produkt aus Benzol-Petroläther umkristallisiert. Wir erhielten 1.3 g Phenylhydrazon des 2-Oxypropylaldehyds in gelben Nadeln von Schmp. 119–120°.

Anal. Gef.: N, 17.35. Ber. für $C_9H_{12}ON_2$: N, 17.06.

Der Mischschmelzpunkt von phenylhydrazon des 2-Oxypropylaldehyds mit dem authentischen Produkt zeigt keine Depression.

2-Oxypropylaldehyd.—Die Darstellung des Aldehyds erfolgte nach der Vorschrift von Nef[11]. 10 g Acrolein wurden mit 14 g Wasser im Einschmelzrohre auf 100° 10 Stunden lang erhitzt. Nach dem Enternen der unveränderten Materialien erhielt man 5 g 2-Oxypropylaldehyd von Sdp. 70–75° (10 mm). n_D^{20} 1.4900.

Phenylhydrazon.—Aus Benzol-Petroläther gelbe Nadeln von Schmp. 119–120°.

Anlagerung von Thiosäure an Monoaddukt (I, R=Ac).—Eine Mischung von 2 g Monoaddukt, 2 g Thiosäure und 0.02 g Azo-bis-isobuttersäurenitril wurde in einem zugeschmolzenen Reaktionsrohr 24 Stunden lang UV-Licht wie vorher ausgesetzt und anschliessend im Vakuum destilliert. Nach dem Entfernen der unverbrauchten Materialien erhielt man 0.9 g Diaddukt (31%) von Sdp. 90–95° (10^{-2}mm).

Anal. Gef.: S, 25.20. Ber. für $C_9H_{14}O_4S_2$: S, 25.58%.

Anlagerung von Äthylmercaptan an Monoaddukt (I, R=Ac).—Eine Mischung von 2 g Monoaddukt, 2 g Äthylmercaptan und 0.02 g Azo-bis-isabuttersäurenitril wurde UV-Licht 24 Stunden lang wie vorher ausgesetzt. Man erhielt 1 g (37%) einer schwach gelben Flüssigkeit, 2-Äthylthio-3-acetoxythio-propylacetat von unangenehmen Geruch. Sdp. 110–115° (1 mm), n_D^{20} 1.5091.

Anal. Gef.: C, 45.97; H, 7.06; S, 27.00. Ber. für $C_9H_{16}O_3S_2$: C, 45.76; H, 6.83; S, 27.09% (Absorptionsspektrum: siehe Abb. 1).

Anlagerung von Thiosäure an Propargylalkohol.—Eine Mischung von 5.6 g Propargylalkohol, 15.2 g Thiosäure und 0.1 g Azo-bis-isobuttersäurenitril wurde UV-Licht wie vorher ausgesetzt. Man erhielt 13 g Monoaddukt (10%) und 13 g Diaddukt (63%).

(a) Monoadduckt, 3-Oxyprop-1-enylthioacetat (I, R=H).—Sdp. 57° (10^{-2}mm) n_D^{11} 1.5280.

Anal. Gef.: C, 45.10; H, 6.25; S, 24.22. Ber. für $C_5H_8O_2S$: C, 45.45; H, 6.10; S, 24.22%.

Die Verbindung ist ein gelbes Öl. Behandelt man 1 g Monoaddukt mit 2.5 g phenylhydrazin wie vorher, so erhält man 0.7 g phenylhydrazon des 2-Oxypropylaldehyds, dessen Schmp. 119–120° ist.

Anal. Gef.: N, 17.35. Ber. für $C_9H_{12}ON_2$: N, 17.30%.

(b) Diaddukt, 2,3-Diacetylthio-propanol (II, R=H).—Sdp. 85–90° (10^{-2}mm), n_D^{25} 1.5159.

Anal. Gef.: C, 40.80; H, 5.87; S, 30.74. Ber. für $C_7H_{12}O_3S_2$: C, 40.39; H, 5.81; S, 30.74%. Die Verbindung ist ein gelbes Öl, dessen Geruch unangenehm und scharf ist.

2,3-Dithiopropanol aus Diaddukt (II, R=H).—15 g Diaddukt wurden mit 100 ccm 1 proz. salzsaurem Methanol 6 Stunden lang auf 60° erhitzt. Das nach dem Entfernen des salzsauren Methanols zurückgebliebene Produkt wurde der Destillation im Vakuum unterworfen. Man erhielt 6 g, 2,3-Dithiopropanol von Sdp. 57° (10^{-2}mm).

Anal. Gef.: S, 51.47. Ber. für $C_3H_5OS_2$: S, 51.64%.

Anlagerung von Thiosäure an Propargylborat.—Ein Gemisch von 8.6 g Propargylborat, 7.8 g Thiosäure und 0.1 g Azo-bis-isobuttersäurenitril wurde wie oben behandelt. Nach Verseifung mit 50 ccm Wasser wurde das Produkt der Destillation unterworfen. Man erhielt 8 g 3-Oxyprop-1-enylthioacetat von Sdp. 60–61° (10^{-2} mm).

Anal. Gef: S, 24.14. Ber. für. $C_5H_8O_2S$: S, 24.22%.

Wir möchten hier dem Kultus-ministerium für die Gewährung einer Unterstützung zur Anregung wissenschaftlicher Forschung Dank sagen, ebenso Herrn A. Kondoh und N. Yamazaki für die Ausführung der Mikroanalysen.

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14) Fischer, *Ann.*, **190**, 129 (1878).

A Thermistor Method for the Determination of Velocity Coefficients of Vinyl Polymerization. V. The Effect of the Bulk Viscosity on the Velocity of Vinyl Polymerization

By Hajime MIYAMA

(Received December 10, 1956)

Introduction

It is well known that the ratio of the propagation constant to the termination constant k_p/k_t for vinyl polymerization increases with the increase of the degree of conversion[1-4]. Apparently this is a result of the increasing bulk viscosity of the reaction system causing the mobility of monomer M and radical M_n* to slow down. However, no experiment to measure both k_p/k_t and the bulk viscosity η to obtain the relation between these values has been conducted and only M.F. Vaughan's theory[5] for the thermal polymerization of styrene is related to the subject.

The author therefore measured those two values by using a special reaction vessel, which could function as a viscosimeter, compared the results of measurements with the values of k_p and k_t of vinyl acetate given in the 4th paper[1] of this series, and obtained the general formula which gives the relation between η and k_p or k_t.

Theoretical

The theoretical formula, postulated by E. Rabinowitch[6], expresses the effect of the bulk viscosity on the rate constant in the liquid reaction. If liquid can be assumed to possess a quasicrystalline structure, the rate constant c (1.molecule^{-1}.sec^{-1}) for a second-order reaction between two molecules of the same size as the solvent molecules, is

$$c=n\nu\exp(-E/RT)/N_0[1+a^2Y\nu\exp(-E/RT)/2D] \quad (1)$$

where $D=D_A+D_B$, D_A and D_B are the diffusion constants of the two molecules, E is the activation energy, a is the shortest distance between lattice points, n is the co-ordination number of the lattice, ν is the frequency factor, N_0 is the number of lattice points and Y is constant (ca. 2). From this equation Vaughan[5] derived the following approximate formula for the velocity constant k(1 mole.$^{-1}$ sec^{-1}) of the polymerization of styrene.

$$k=\nu\exp(-E/RT)/[1+a^2\nu\exp(-E/RT)/D]=k_0/(1+Q/D) \quad (2)$$

where $k_0=\nu\exp(-E/RT)$ and $Q=a^2k_0$.

By the application of this formula to the reaction between monomer M and radical M_n*, the propagation process of polymerization was explained and by its application to the reaction between radicals, the termination process was explained. The equation (2) equals, the following equation

$$k_0/k=1+Q/D \quad (3)$$

If the functional relation between D and η be put as

$$1/D=f(\eta) \quad (4)$$

then

$$k_0/k=1+Qf(\eta) \quad (5)$$

Although Vaughan used the Einstein-Stokes' relation as the relation (4), it is doubtful that Einstein-Stokes' relation is applicable for a complex system such as the system of polymerization. Moreover, the validity of the application of the equation (1) seems doubtful because in the propagation and termination process of polymerization, one or both of two reacting molecules is larger in size than the solvent molecules (monomers).

When the reacting molecules are larger than the solvent molecules, the following

1) H. Miyama, This Bulletin, **29**, 711, 715, 720 (1956); **30**, 10 (1957).
2) W. I. Bengough and H. W. Melville, *Proc. Roy. Soc.*, **A230**, 429 (1955).
3) S. Fujii, This Bulletin, **27**, 216, 238 (1954).
4) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); **73**, 1700, 5395 (1951).
5) M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).
6) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

relation postulated by M. von Smoluchowski[7] is applicable:

$$ {}_AZ_B = 2\pi(D_A+D_B)(r_A+r_B)N/1000 = 2\pi N(r_A+r_B)D/1000 \quad (6) $$

where ${}_AZ_B$ (1.mole^{-1}.sec^{-1}) is the collision number between two molecules A and B, when the concentrations of two molecules are a unit, r_A and r_B are diameters of each molecules and N is Avogadro's number. If it is assumed that only the factor ${}_AZ_B$ of k varies with the variation of the bulk viscosity, then the following relation can be derived

$$ k_0/k = D_0/D = D_0 f(\eta) \quad (7) $$

Experimental

By obtaining experimentally the relation between η and k_p/k_t, it is possible to ascertain whether (5) or (7) is applicable for vinyl polymerization. Details of this experiment are as follows:

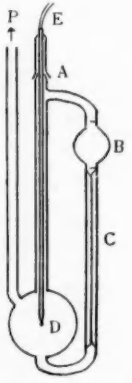

Fig. 1. Reaction vessel.
A; Joint
B, C; Viscosimeter
D; Thermistor
E; Thermistor's lead wires
P; To vacuum

The reaction vessel, shown in Fig. 1, made of soft glass and equipped with a thermistor, is ca. 19 cc. in capacity. Its inside diameter is 40 mm. and the inside depth is 15 mm. This vessel can be connected to the vacuum system at P. The lead wires of the thermistor are covered by very thin soft glass tubing which is sealed at the upper end of joint A. The glass bulb B is ca. 5 cc. in capacity. At its both ends two lines are marked. The capillary C is 10 cm in length and 2.5 mm. in diameter. Using this vessel, the values of k_p/k_t can be measured by the method described in the previous papers[1], and at the same time, the bulk viscosity is obtainable by turning the vessel upside down to transfer the sample into the bulb B, then righting the vessel and measuring the time for the sample to pass between the two marks.

Other experimental procedures and the method of purification of sample and sensitizer are the same as in the previous papers[1]. But the effect of the direct irradiation of light on the thermistor was not observed, because the vessel is made of soft glass and has larger loss in transmission of light than the quartz vessel used in the first paper[1].

Results

The measurement was accomplished on methyl

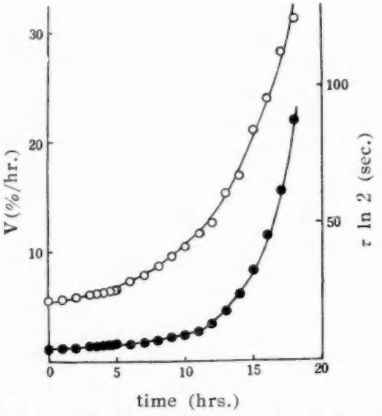

Fig. 2. The variation of rate and lifetime with time for the polymerization of methyl methacrylate.
○ V; ● τ ln 2

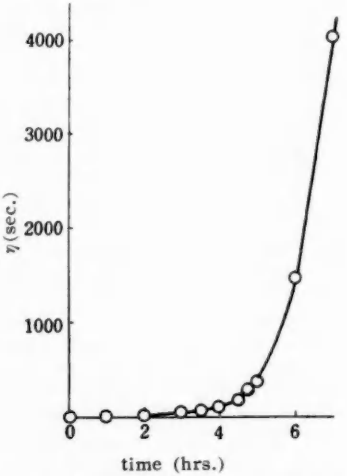

Fig. 3. The variation of bulk viscosity with time for the polymerization of methyl methacrylate.

7) M. von Smoluchowski, *Z. Physik. Chem.*, **92**, 129 (1918).

methacrylate and vinyl acetate at 30°C by using 1,1'-azo-biscyclohexanecarbonitrile as a photosensitizer, the concentration of which was 0.013 mole/l in methyl methacrylate and 0.002 mole/l in vinyl acetate.

The variation of the velocity V and the lifetime τ for the polymerization of methyl methacrylate during continuous polymerization are shown in Fig. 2. The variation of the bulk viscosity η (the time measured by viscosimeter) is shown in Fig. 3. By calculating the degree of conversion φ (%) and the values of k_p/k_t as described in the 3rd paper[1] of this series, Table I was obtained.

TABLE I

THE VARIATION OF η AND k_p/k_t WITH CONVERSION FOR THE POLYMERIZATION OF METHYL METHACRYLATE

Conversion	η(sec.)	$(k_p/k_t)\times10^5$
0	1.3	0.99
0.6	4.1	1.01
1.1	11.5	1.12
1.7	33.0	1.23
2.0	53.8	1.30
2.3	99.4	1.38
2.7	185.1	1.40
2.8	286.5	1.48
3.0	365.2	1.54
3.7	1456.1	1.80
4.4	4030.0	2.22
5.2		2.60
6.2		3.34
7.2		4.04
8.2		5.22
9.4		7.21
10.8		12.1
12.4		18.1
14.3		32.0
16.6		53.6
19.2		85.5
22.1		121.0

The value of k_p/k_t over 22% conversion was not obtainable, because the lifetime was very long and the measurement was impossible. As shown in this table, the increase of k_p/k_t with the degree of conversion is more remarkable than those for other monomers. This result coincides with the results obtained by other methods[3,4]. The increase in the bulk viscosity is more remarkable than the increase of k_p/k_t, but the measurement of the viscosity over conversion 4.4% was impossible, because it took a long time and was not reproducible.

Because details of measurements on the vinyl acetate have already been described in the third paper[1], these are omitted and only their results are shown in Table 2. The measurement of the viscosity over 16.1% was impossible.

TABLE II

THE VARIATION OF η AND k_p/k_t WITH CONVERSION FOR THE POLYMERIZATION OF VINYL ACETATE

Conversion(%)	η(sec.)	$(k_p/k_t)\times10^5$
0	1.0	1.20
1.2	1.4	1.22
2.4	2.1	1.26
3.6	7.5	1.31
4.9	16.9	1.37
6.2	32.7	1.43
7.5	65.0	1.49
8.9	116.5	1.53
10.3	183.1	1.56
10.7	343.5	1.64
13.1	707.7	1.72
14.6	976.1	1.88
16.1	1734.0	2.10
20.8		2.63
28.8		3.50
37.3		4.89
45.5		6.15
53.2		11.0
60.0		18.2
68.1		35.8

Discussion

Let the ratio of the viscosity η at any conversion to η_0 at 0 conversion and the same ratio of k_p/k_t be x and y respectively, i. e.

$$\left.\begin{aligned} x &= \eta/\eta_0 \\ y &= (k_p/k_t)/(k_p/k_t)_0 \end{aligned}\right\} \quad (8)$$

Although the measurement of the viscosity was impossible at high conversion, the following relations were observed between

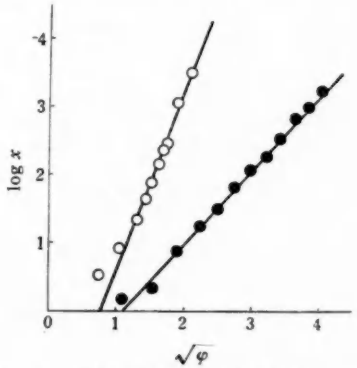

Fig. 4. The variation of $x=\eta/\eta_0$, with conversion φ.
○ Methyl Methacrylate
● Vinyl Hatate

x and φ at low conversion of polymerization as shown in Fig. 4, i. e. on methyl methacrylate,

$$\log x = 2.68\sqrt{\varphi} - 2.17 \qquad (9)$$

and on vinyl acetate

$$\log x = 1.11\sqrt{\varphi} - 1.22 \qquad (10)$$

These relations are in good agreement with the relation suggested by R. S. Spencer and J. L. Williams[8], in which the bulk viscosity is proportional to $\exp\sqrt{W}$, where W is the weight fraction of polymer. Then the values of the bulk viscosity at high conversion, though not measurable, can be calculated by using (9) and (10). In Table 3, the values of x and y are tabulated.

TABLE III

THE VALUES OF x AND y FOR THE POLYMERIZATION OF METHYL METHACRYLATE AND VINYL ACETATE

Methyl Methacrylate		Vinyl Acetate	
x[a]	y	x[a]	y
1.0	1.00	1.0	1.00
3.2	1.02	1.4	1.02
8.3	1.13	2.1	1.05
25.4	1.24	7.5	1.09
41.4	1.31	16.9	1.14
76.3	1.39	32.7	1.19
142.8	1.41	65.0	1.24
221.0	1.49	116.5	1.28
281.5	1.56	183.1	1.30
1121.0	1.82	343.5	1.37
3100.0	2.24	707.7	1.44
$10^{3.96}$	2.62	976.1	1.57
$10^{4.50}$	3.37	1734.0	1.75
$10^{4.92}$	4.08	$10^{4.05}$	2.19
$10^{5.91}$	5.27	$10^{4.74}$	2.92
$10^{6.05}$	7.29	$10^{5.57}$	4.07
$10^{6.68}$	12.2	$10^{6.28}$	5.12
$10^{7.25}$	18.3	$10^{6.90}$	9.17
$10^{8.00}$	32.4	$10^{7.42}$	15.2
$10^{8.72}$	54.2	$10^{7.94}$	29.2
$10^{9.61}$	86.5		
$10^{10.45}$	122.2		

a) In this Table exponential figures are calculated by equations (9) or (10).

Because k_p is constant at the initial stage (until φ=30—40%) of polymerization and the increase of k/k_t with the degree of conversion depends mainly upon the decrease of k_t[1-4], y in equation (8) at this stage equals to $(k_t)_0/k_t$, i. e.,

$$y = (k_t)_0/k \qquad (11)$$

8) R. S. Spencer and J. L. Williams, *J. Colloid Sci.*, **2**, 117 (1947).

As shown in Figs. 5 and 6, the following relations at the initial stage of polymerization, for methyl methacrylate may be derived:

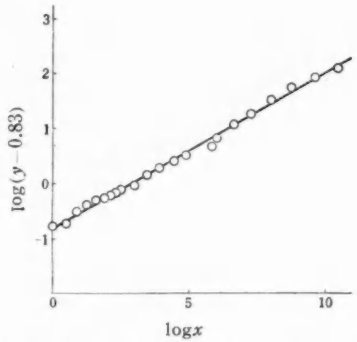

Fig. 5. The variation of y with x for the polymerization of methyl methacrylate.

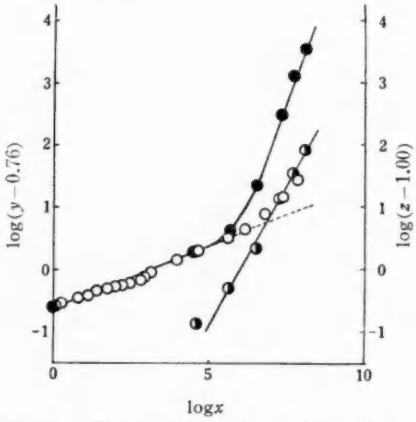

Fig. 6. The variation of y and z with x for the polymerization of vinyl acetate.
○, $y=(k_p/k_t)/(k_p/k_t)_0$;
●, $y=(k_t)_0/k_t$
◑, $z=(k_p)_0/k_p$

$$y = 0.83 + 0.17x^{0.28} \qquad (12)$$

and for vinyl acetate

$$y = 0.76 + 0.24x^{0.20} \qquad (13)$$

Because k is not constant at the later stage of polymerization and $(k_t)_0/k_t$ is not equal to $(k_p/k_t)/(k_p/k_t)_0$, it is necessary to consider k_p and k_t separately. Using the values of the viscosity in this report, it is possible to obtain the relation between the bulk viscosity and k_p or k_t, which was presented on vinyl acetate in the 3rd paper[1] of this series. Since these values

of k_p and k_t were measured at 20°C, these were corrected to 30°C by using the values of the activation energies E_p and E_t given in the 4th paper[1]. Although the variation of y with x at the initial stage obeys the equation (13) as shown in Fig. 6, it is replaced by the relation $y \propto x^{1.5}$ at the later stage. The following equation therefore is applicable throughout the total process of polymerization.

$$y=0.76+0.24(x^{0.20}+10^{-8}x^{1.50}) \quad (14)$$

Let the ratio of $(k_t)_0$ to k_t be z, i. e.

$$z=(k_p)_0/k_p \quad (15)$$

Then the following equation is obtainable from Fig. 6 throughout the total process of polymerization,

$$z=1+0.65\times10^{-6}x \quad (16)$$

As shown in Table IV, there is a good agreement between the calculated values of y or z by using equation (14) or (16) and the experimental values.

TABLE IV
THE COMPARISON OF CALCULATED VALUES WITH EXPERIMENTAL VALUES ON y AND z FOR THE POLYMERIZATION OF VINYL ACETATE

Conversion (%)	x	y(exp.)	y(calc.)	z (exp.)	z (calc.)
0	1	1.00	1.00	1.00	1.00
28.15	$10^{4.68}$	2.64	2.85	1.14	1.03
39.00	$10^{5.71}$	4.82	4.33	1.50	1.33
49.80	$10^{6.61}$	23.8	26.2	3.38	3.64
59.30	$10^{7.33}$	337	248	14.9	14.9
66.40	$10^{7.73}$	1250	966	35.5	35.9
71.10	$10^{8.15}$	3780	3991	91.8	92.8

From the comparison of (14) with (7), the following equation is obtained:

$$(k_t)_0/k_t=(D_R)_0/D_R$$
$$=0.76+0.24(x^{0.20}+10^{-8}x^{1.50}) \quad (17)$$

And from the comparison of (16) with (7)[9],

$$(k_p)_0/k_p=(D_M)_0/D_M=1+0.65\times10^{-6}x \quad (18)$$

where D_M and D_R are the diffusion constants of monomer M and radical M_n* respectively. There is no direct measurement of the diffusion constant of monomer, but Melville et al.[2] estimated its value by measuring the diffusion velocity of α,α'-diphenylpicrylhydrazil in the various conversions of vinyl acetate. Comparison of these values of $(D_M)_0/D_M$ with the values of η/η_0 of this report is shown in Fig. 7. Here it is apparent that the measured values of $(D_M)_0/D_M$ obey the relation (18). This result shows that the application of (7) is reasonable. At the same time, the

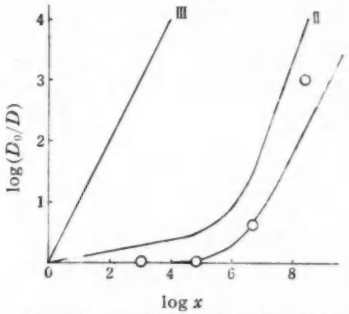

Fig. 7. The variation of D_0/D with x
I, $D_0/D=1+0.65\times10^{-6}x$;
II, $D_0/D=0.76+0.24(x^{0.20}+10^{-8}x^{1.50})$;
III, $D_0/D=x$;
○, The measured values of D_0/D

relation (17) is shown in Fig. 7 and the shape of this curve is similiar to the curve (18), except that $(D_R)_0/D_R$ increases with the increase in the bulk viscosity at rather low viscosity. It seems probable that the effect of the bulk viscosity is more remarkable on the diffusion constant of the radical than on that of the monomer.

If the Einstein-stoke's relation adopted by Vaughan is applicable, $(D_M)_0/D_M$ may be expressed in a different form from (18), i.e.

$$(D_M)_0/D_M=x \quad (19)$$

The measured values of $(D_M)_0/D_M$ deviate greatly from this relation. On the other hand, if $a\fallingdotseq3\times10^{-8}$cm.[6], $k_0\fallingdotseq5\times10^{2}$ [1] and $D_0\fallingdotseq10^{-5}$ cm^2.sec^{-1} [5] are used in the Vaughan's equation (3), the values of Q becomes ca. 5×10^{-13} and from the comparison of (3) with (16), $(D_M)_0/D_M$ equals ca. 10^2x.

$$(D_M)_0/D_M=10^2x \quad (20)$$

This result (20) is more unsatisfactory than the equation (19) for the measured values of $(D_M)_0/D_M$. Therefore the application of (5), (3) and (1) is not considered reasonable. The reason why Vaughan's qualitative application of the equation (1) for the polymerization of styrene gave apparently valid results may be his rather arbitrary selection of the values of the diffusion constants and the

9) Although $D=D_M+D_R$ in the propagation process, it seems reasonable to assume $D\fallingdotseq D_M$ because $D_M \gg D_R$.

use of an assumed relation $1/D \propto \eta$.

From the above discussion, it seems that the application of (7) and (6) is more reasonable than (5) and (1) for the propagation and termination process of polymerization, in which the reacting molecules are far larger than the solvent molecules. But to prove this conclusion absolutely, it is necessary to measure the bulk viscosity at high conversion and the diffusion constants of monomer and radicals, though they are not measurable in this study.

Summary

The author measured the ratio of the propagation constant to the termination constant k_p/k_t and the bulk viscosity η of the reaction system for the polymerization of methyl methacrylate and vinyl acetate by using the thermistor method and a special reaction vessel, which could be used as a viscosimeter, then compared the results of these measurements with the values k_p and k of vinyl acetate presented in the previous paper[1], and thus obtained the general formula for the relation between the bulk viscosity and k_p or k. The obtained results are summarized as follows;

1) Throughout the total procss for the polymerization of vinyl acetate the relation between the termination constant k_t and η is expressed as follows,

$$(k_t)_0/k_t = 0.76 + 0.24[(\eta/\eta_0)^{0.20} + 10^{-8}(\eta/\eta_0)^{1.50}]$$

In case of methyl methacrylate, the following formula is recommended which holds up to 22% conversion.

$$(k_t)_0/k = 0.83 + 0.17(\eta/\eta_0)^{0.28}$$

Where $(k_t)_0$ and η_0 are the values of k_t and η at conversion 0.

2) The propagation constant k_p and η in the polymerization of vinyl acetate are expressed as follows.

$$(k_p)_0/k = 1 + 0.65 \times 10^{-6}(\eta/\eta_0)$$

3) These results can be explained by the assumption that k_t and k_p are proportional to the diffusion constants of reacting molecules. Using the theory of Rabinowitch-Vaughan, we find some difficulties to explain our experimental results.

The author wishes to express his sincere thanks to Dr. Momotaro Suzuki of this Academy for his helpful advice and encouragement and Mr. Shinichi Taira of Tokyo Metropolitan University for his kind supply of 1,1'-azo-biscyclohexanecarbonitrile.

Department of Chemistry, Defense Academy, Yokosuka

Surface Chemistry of High Polymers. VII[1] *Polyacids and Some Vinyl Polymers*

By Hiroshi HOTTA* and Toshizo ISEMURA

(Received December 12, 1956)

As mentioned in the previous paper[2], the study of polyelectrolytes has many interesting points not only for pure physical chemistry but also as an important model of biocolloidal substances. Therefore, some investigations have been carried out along these lines. Especially, the solution of polymethacrylic acid has been studied exhaustively as a typical linear polyelectrolyte[3]. However, the surface film of polyelectrolytes has not been studied thoroughly as yet. In the present experiment, the films of poly-L-glutamic acid and of the copolymer of maleic acid and vinyl acetate were studied at the air/ and oil/water interfaces by measuring their interfacial pressure and potential in order to know the behavior of carboxyl groups as the most important component of polyelectrolytes. The interfacial

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1) Part VI of this series, H. Hotta, This Bulletin, **28**, 64 (1955).

2) T. Isemura, H. Hotta and S. Otsuka, ibid., **27**, 93 (1954).

3) For example, A. Katchalsky, O. Künzel and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1950); A. Katchalsky, ibid., **7**, 393 (1951).

potential of some non-electrolytic linear polymers and di- and tri-carboxylic acids was also measured for reference in order to elucidate the behavior of the present polyacids. The obtained results were considered in the light of the knowledge of some polyacids, which had been studied previously[2,4,5].

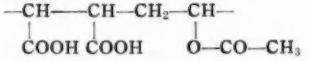
Experimental

The films were spread at the air/and petroleum ether (b. p. 90–130°C)/aqueous phase interfaces, and their interfacial pressure and potential were measured at room temperature. The pH of aqueous phase was adjusted by hydrochloric acid. The apparutus and methods were the same as in the previous papers[2,4].

Materials and spreading solutions used in the present investigation were as follows. The copolymer of maleic acid and vinyl acetate, which was kindly supplied from Sekisui Chem. Ind. Co., Ltd., and polyvinyl alcohol, whose degree of polymerization was 2510, were dissolved in distilled water. Poly-L-glutamic acid, which was the same as that studied previously in our laboratory[6], was dissolved in N/100 sodium hydroxide solution. Isopropyl alcohol was added to all these solutions in the concentration of 20% to help the spreading. Polyvinyl acetate[7], octadecyl malonic acid[6] and hexadecane-1,1,2-tricarboxylic acid[6] were dissolved in the same solvent as in the previous studies, respectively.

Results

We studied first the film of the copolymer of maleic acid and vinyl acetate on the aqueous phase of various pH. Since this copolymer, which is called hereafter MAVA, has



as a constitutional unit, figures for this copolymer in the present paper are plotted against the

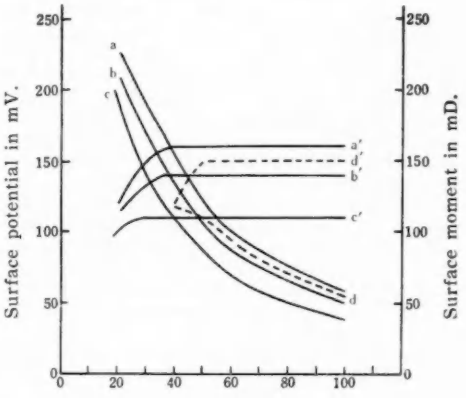


Fig. 2. The interfacial potential (moment)-area curves of MAVA at the air/water interface (curve a pH 1.6 and 2.6, curve b pH 3.2 and curve c pH 3.8), and at the petroleum ether/water interface (curve d pH 1.6 containing 2 M KCl) (at about 18°C).

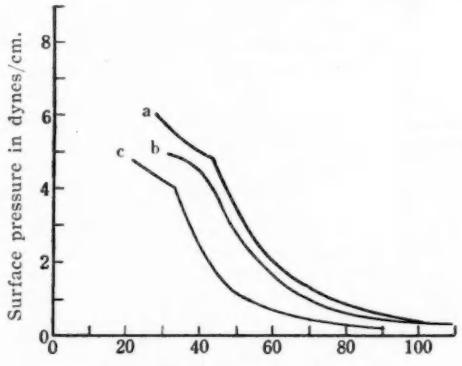


Fig. 1. The surface pressure-area curves of MAVA at the air/water interface (at about 15°C);
curve a (pH 1.6–4.0), curve b (pH 4.4), and curve c (pH 5.2).

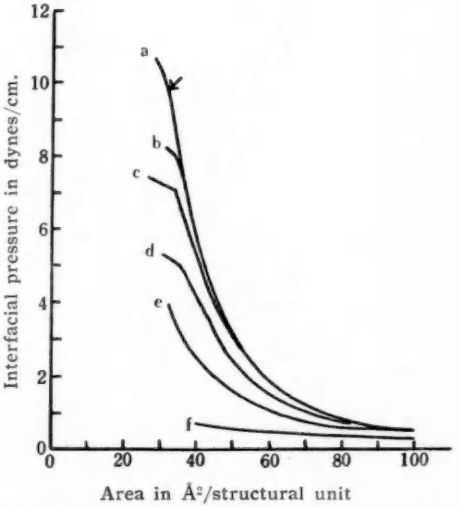


Fig. 3. The interfacial pressure--area curves of MAVA at the petroleum ether/water interface at about 20°C; curve a pH 1.6 and 2.4, curve b pH 2.8, curve c pH 3.2, curve d pH 4.0, curve e pH 4.8 and curve f pH 5.6.

4) H. Hotta, This Bulletin, **27**, 412 (1954).
5) H. Hotta and T. Isemura, ibid., **29**, 90 (1956).
6) T. Isemura and K. Hamaguchi, ibid., **27**, 339(1954).
7) T. Isemura, H. Hotta and T. Miwa, ibid., **26**, 380 (1953).

area per this unit. The surface pressure and potential at the air/water interface are shown in Figs. 1 and 2, respectively. The corresponding surface moment-area curves in the present paper are represented by prime in the same figure of surface potential. The observed value of surface potential, which will be mentioned later in Fig. 8, was somewhat various, and this tendency was considerable at pH more than 4.0.

The interfacial pressure of MAVA at the petroleum ether/water interface is shown in Fig. 3. The kink point of curve a is shown by an arrow. Curve a of this figure coincides entirely with curve a in Fig. 1 at the moderate area. It means that MAVA gives a film of expanded type like polyvinyl acetate even at the air/water interface[8]. The spreading solution dissolved partially into aqueous phase at the lower pH than at the air/water interface. (See Figs. 1 and 3.) Since the distinct interfacial potential-area curve could not be obtained in the higher pH range at the oil/water interface, only the results on the aqueous phase of pH 1.6 containing 0.2 M potassium chloride is shown with dotted line (curve d) in Fig. 2. In Fig. 2, the surface moments at both interfaces are nearly equal to each other. This is another evidence that MAVA is of expanded state even at the air/water interface, for the film could not have the same configuration, namely, the same surface moment, if it were the film of different type at both interfaces.

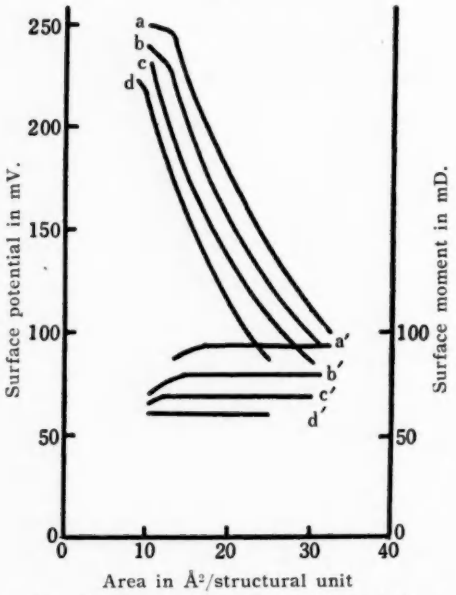


Fig. 4. The surface potential (moment)-area curves of poly-L-glutamic acid at the air/water interface at about 23°C; curve a pH 1.2 and 3.8, curve b pH 4.2, curve c pH 4..8 and curve d pH 5.2.

8) H. Hotta, *J. Colloid Sci.*, **9**, 504 (1954).

The surface potential-area curves of poly-L-glutamic acid at the air/water interface are shown in Fig. 4. The surface pressure and viscosity of this polyaminoacid had been reported previously from our laboratory[6]. The reproducible curve could not be obtained at the larger area than 30 Å² per residue. Since the interfacial potential-area curve of poly-L-glutamic acid at the oil/water interface could not be obtained due to the partial dissolution of spreading solution into aqueous phase, only the maximum interfacial potential is shown as the function of the pH of aqueous phase in Fig. 5. Nevertheless, the interfacial moment on pH 1.6 might be about 80 mD. The dependence of the maximum interfacial potential on the pH of aqueous phase is similar at both interfaces. (See Figs. 4 and 5.)

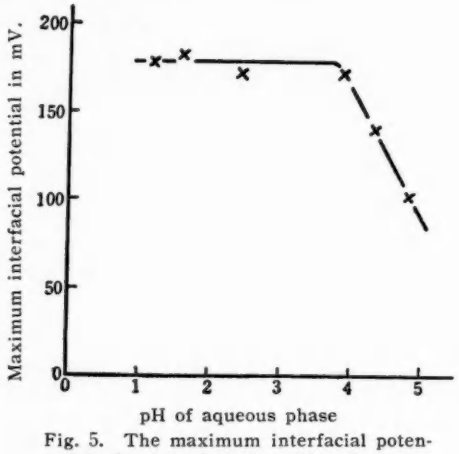


Fig. 5. The maximum interfacial potential of poly-L-glutamic acid at the petroleum ether/water interface on the various pH of aqueous phase.

As the example of simple polyacid, we measured the surface potential of octadecyl malonic acid and hexadecane-1,1,2-tricarboxylic acid at the air/water interface (pH 1.6). The surface moments obtained at the larger area are shown in Table I, although the values at the smaller area than 60 Å² per molecule show some irregularity. The surface pressure-area relation of these acids had been reported in the preceding paper[5].

On the other hand, we measured the interfacial potential of polyvinyl acetate and polyvinyl alcohol at the petroleum ether/water interface for reference. The result of polyvinyl acetate is shown in Fig. 6, together with the curve at the air/water interface in the previous paper[7]. Since the potential values at the kink point of curves a and b (422 mV.) are quite identical, the true curve at the oil/ water interface may be expected as shown with dotted line, if we take imperfect spreading at the smaller area at this interface into consideration. The interfacial pressure and potential of polyvinyl alcohol at the oil water interface is shown in Fig. 7. The change of interfacial pressure with time appeared at the smaller area than

TABLE I

THE SURFACE MOMENT OF VARIOUS COMPOUNDS

Compound	Formula	Surface Moment in mD at Air/Water Interface	Surface Moment in mD at Oil/Water Interface	Reference
Polyvinyl alcohol	$-CH_2-CH(OH)-$	40	45	12, The present
Polymethacrylic acid	$-CH_2-C(CH_3)(COOH)-$	90	15	2, 4
Poly-4-vinyl benzoic acid	$-CH_2-CH(C_6H_4COOH)-$	100	—	9
Poly-L-glutamic acid	$-NH-CH(CH_2CH_2COOH)-CO-$	95	80	The present
Poly-ε-caproamide	$-NH-(CH_2)_5-CO-$	225	—	10
Copolymer of maleic acid and vinyl acetate	$-CH(COOH)-CH(COOH)-CH_2-CH(OCOCH_3)-$	160	150	The present
Octadecyl malonic acid	$CH_3-(CH_2)_{17}-CH(COOH)-COOH$	240	—	The present
Hexadecane-1, 1, 2-tricarboxylic acid	$CH_3-(CH_2)_{16}-CH(COOH)-CH(COOH)-COOH$	200	—	The present
ω-ω'-hexadecane-dicarboxylic acid	$HOOC-(CH_2)_{16}-COOH$	350	—	11
Polyethylene terephthalate	$-O-CO-C_6H_4-CO-O-(CH_2)_2-$	350	—	1
Polyvinyl acetate	$-CH_2CH(OCOCH_3)-$	340[a] / 280[b]	280	7, The present
Polymethyl methacrylate	$-CH_2C(CH_3)(COOCH_3)-$	250	—	10
Polyoctadecyl methacrylate	$-CH_2-C(CH_3)(COOC_{18}H_{37})-$	460	—	12
Myristic acid	$CH_3-(CH_2)_{12}-COOH$	156[a] / 250[b]	—	13

a) An expanded state.
b) A condensed state.

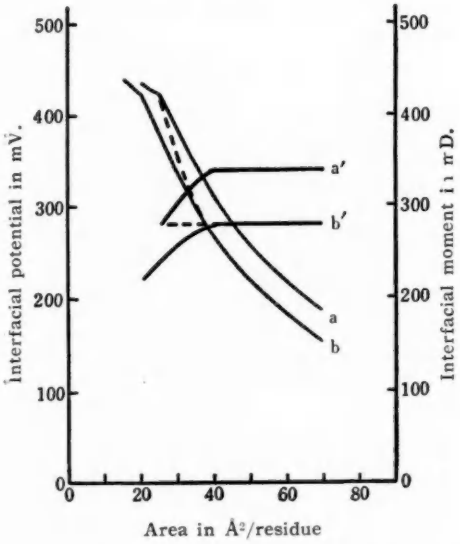


Fig. 6. The interfacial potential (moment)-area curves of polyvinyl acetate at the air/water (curve a) and petroleum ether/water (curve b) interfaces.

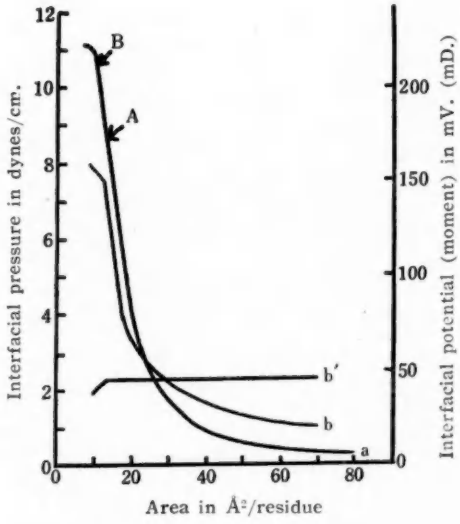


Fig. 7. The interfacial pressure-area curve a and potential (moment)-area curve b of polyvinyl alcohol at the petroleum ether/water interface.

13 Å² per monomer (arrow A), where the interfacial moment began to lower. Furthermore, the lowering of the pressure becomes more distinct in the region of the area smaller than 11 Å² per monomer (arrow B).

Discussion

As mentioned above, the copolymer of maleic acid and vinyl acetate (MAVA) on pH 1.6 gives a film of expanded type even at the air/water interface. On the other hand, at the air/water interface, polymethacrylic acid gives a film of condensed type on the aqueous phase of pH 1.6 due to cohesion between carboxyl groups[2], and polyvinyl acetate gives a film of expanded type due to the effect of short side chains[7,8] as shown in the previous investigations. It seems that the short side chains in this copolymer still play a role of two dimensional self-plasticizer against cohesion between carboxyl groups.

In the previous paper[5] it was proposed that, when n_{atom} is defined by an equation

$$n_{atom} = a\left(\frac{kT}{\pi A}\right)_{A\to\infty}$$

where a is the number of main atoms in the structural unit of main chain, k Boltzmann's constant, T absolute temperature, π interfacial pressure, A area per structural unit, n_{atom} is a characteristic quantity representing the behavior at the interface. The value of n_{atom} for MAVA was found to be 43, which corresponds to the mean value of 38 for polyvinyl acetate and 48 for methacrylic acid in the previous investigations[8]. The value for polyvinyl alcohol was 41.

Since the surface moment of some compounds was measured in the present investigation, we have made a list of them in the non-ionized state or of non-electrolyte with those of other related compounds[9-13] in Table I, in which the value of surface moment is for the represented formula. It may be assumed that the compounds, whose surface moment is nearly equal at both interfaces, have almost the same orientation at both interfaces. For polyvinyl acetate, the moment at the oil/water interface is identical with that at the air/water interface not at the expanded state but at the compact state. It is understood in the light of a previous model[8,10] on account of the affinity of methyl group to oil phase.

The surface moments of carboxyl groups for the polymers examined are quite different as shown in Table I. It might be due to the various orientations of C=O bond as mentioned previously[8,10] Generally speaking, it appears that the horizontal orientation of a chain directly linking to the carbon atom of carboxyl group makes the surface moment lower, and that this tendency of lowering is more predominant for the closer approach of carboxyl groups with each other (for example, hexadecane-1,1,2-tricarboxylic acid). The surface moment of MAVA and of poly-L-glutamic acid can not be explained by the additivity of the constituent polar groups cited in Table I. (Polymethacrylic acid and polyvinyl acetate for MAVA, or polymethacrylic acid and poly-ε-caproamide for poly-L-glutamic acid) It might be attributed to the change of mutual orientation of these polar groups at the interface.

Besides, we must consider the ionization effect of carboxyl groups for polyacids with increasing pH of aqueous phase. Especially, the surface moment is most sensitive to this effect, and is lowered due to the ionization of the acid group. When the surface moment of polyacids in the range of constant value at the air/water interface are plotted against the pH of aqueous

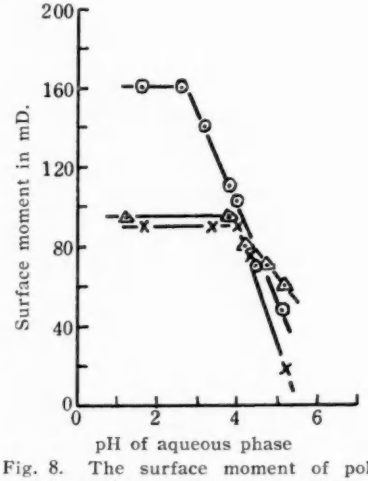


Fig. 8. The surface moment of polyacids at the constant range at the air/water interface plotted against the pH of aqueous phase; MAVA (⊙), poly-L-glutamic acid (△) and polymethacrylic acid (×).

9) I. R. Miller, *J. Colloid Sci.*, **9**, 579 (1954).
10) H. Hotta, This Bulletin, **27**, 80 (1954).
11) H. Hotta and T. Isemura, ibid., **25**, 101 (1952).
12) D. J. Crisp, *J. Colloid Sci.*, **1**, 161 (1946).
13) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.* (London), **130A**, 270 (1931).

phase in Fig. 8, we find that the bending points of these curves correspond almost to the pK of the monomer unit of these polyacids, which is 2.85, 4.25 and 4.85 for malonic acid, glutamic acid and isobutyric acid in this case, respectively. The values of surface moment of MAVA at pH more than 4.0 in Fig. 8 are the mean values of the repeated experiments, for they were various as mentioned above. The curve for polymethacrylic acid is cited from the previous results[3].

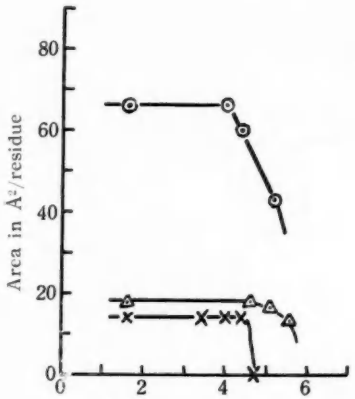


Fig. 9. The area of polyacids at the constant surface pressure (1 dyne/cm.) at the air/water interface plotted against the pH of aqueous phase (at 10–15°C); MAVA (◉), poly-L-glutamic acid (△) and polymethacrylic acid (×).

On the other hand, the similar relationship was not found for surface pressure as shown in Fig. 9, in which the curves for poly-L-glutamic acid[6] and polymethacrylic acid[2] are cited from the previous results. In the case of surface pressure, the contribution of the non-ionizable part might be fairly effective even in the region of larger pH. Although the lowering of these curves with increasing pH is due to the partial dissolution, this would be determined not only by the degree of ionization but also the hydrophylic nature of non-ionizable part and the state of the molecule. It is necessary for complete ionization that the electrostatic repulsion between ionic groups must overcome the intramolecular cohesion (van der Waals' force or hydrogen bonding)[2,8]. All pH's at the point, where the lowering occurs, are between 4 and 5.

It is more or less difficult to obtain the distinct result not only in the ionized state, but also in the non-ionized state for polyacids studied in the present investigation except for polymethacrylic acid which gives a film of condensed type. The surface pressure changes more or less with time. The similar result is reported for polybenzoic acid[9]. It may be caused by the gelation due to hydrated carboxyl groups.

Summary

The films of polyacids (poly-L-glutamic acid and the copolymer of maleic acid and vinyl acetate) and some related compounds were studied in order to know the behaviour of carboxyl groups in the linear polymer at the interface. The principal results obtained are as follows.

The orientation of carboxyl group is affected considerably by other accompanying groups in polymer. Hence, the surface moment of carboxylic compounds is various according to the surface orientation of respective groups in the polymer. Accordingly, the surface moment of copolymer cannot be explained by the simple additivity of the moment of constituent polar groups.

The surface moment of polyacids abruptly decreases nearly at the pH of aqueous phase equal to the pK of corresponding structural unit.

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A Study on the Electric Conductivity of Sodium Silicate Aqueous Solution. III. On the Relationship between Conductance and Viscosity

By Hiroshi UKIHASHI

(Received November 19, 1956)

Introduction

In the previous papers[1,2], the author has remarked that the electric conductivity of sodium silicate solution seemed independent of their viscosity at high concentration range. This has been suggested by the experimental facts that the change of viscosity with concentration varied widely among the solutions having different molar ratio around the concentration where maximum specific conductivity was shown, and that the equivalent conductivity computed theoretically, with viscosity correction, fell increasingly below the observed value above a definite concentration range.

Since conductance in electrolyte solution is a result of the movement of ions under an applied potential, and viscosity is the reciprocal of fluidity which expresses the rate of shear taking place with a definite velocity under unit force, they both can be treated as rate process. Then the comparative study of conductance and viscous flow in view of the theory of rate process is of much value on considering the structure of solution, as it gives some information concerning the bearings on the mechanisms of both phenomena.

In the present report the mechanism of conductance of concentrated sodium silicate solutions of various molar ratio has been discussed in comparison with that of viscous flow from the above mentioned standpoint, and an interpretation has been given for the structure of these solutions.

Experimental

Preparation of sample sodium silicate solutions, apparatus and methods used for the measurement of electric conductivity were described in the preceding paper. Sample solutions for the measurement of viscosity were the same as those for that of the conductance. Viscosity was measured by the capillary method, using Ubbelohde viscometers with varied capillary constants which were originally determined by the maker and calibrated in the author's laboratory, using glycerol solutions of varied concentrations as standards. Measurements were made at a series of increasing temperatures from 5 to 60°C. The relative viscosity was calculated by the usual formula,

$$\eta_{rel} = \frac{t\ (\text{flow time of solution}) \cdot d\ (\text{density of solution})}{t_0\ (\text{flow time of water}) \cdot d_0\ (\text{density of water})}$$

With the concentrated solutions, absolute viscosity was calculated directly by the formula $\eta/d = At$

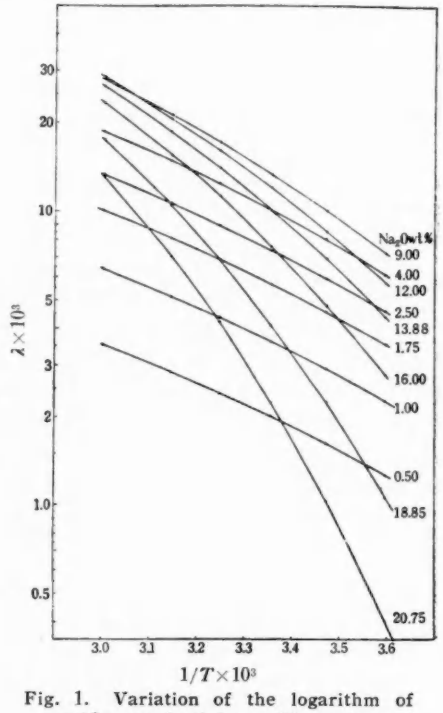


Fig. 1. Variation of the logarithm of specific conductivity with reciprocal of absolute temperature for the 1.00 molar ratio solutions.

1) H. Ukihashi, This Bulletin, **29**, 537 (1956).
2) Idem., ibid, **30**, 414 (1957).

$-B/t$, where A is constant characteristic of capillary, and B constant for kinetic energy correction. It may be conceived that as the concentrated sodium silicate solutions, especially of high molar ratio, would show structural viscosity or thixotropy, the so-called one-point method for the measurement would not be adequate. However, since the present paper has been aimed at discussing primarily the mechanism of electric conductance of sodium silicate solution in relation to that of viscous flow, it would be permissible to set aside, for the present, the problem of exact viscous behavior of the concentrated solution and to leave it for later debate.

Results

Activation Energy of Conductance and Viscous Flow.—In Figs. 1 and 2, the logarithm of specific conductivity was plotted against the

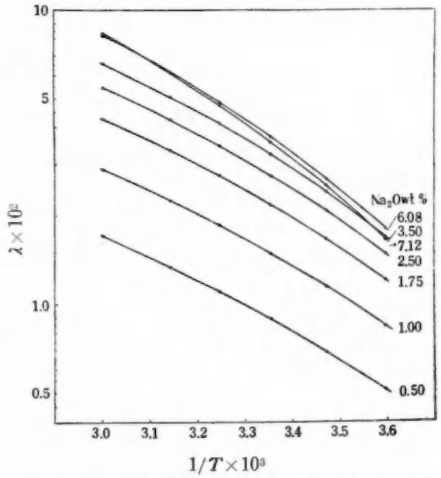


Fig. 2. Variation of the logarithm of specific conductivity with reciprocal of absolute temperature for the 3.95 molar ratio solutions.

reciprocal of absolute temperature for the sodium silicate solutions of molar ratio 1.00 and 3.95. These figures illustrate the different behavior in most marked contrast at various concentrations. The similar curves for viscosity were shown in Figs. 3 and 4 for the corresponding solutions. Although both sets of curves have slight curvature[3], they are regarded as showing approximately linear relationship over a narrow temperature range. The activation energies of conductance and viscous flow are expressed as $d\ln\lambda/d(1/T)=-E_\lambda/R$, and $d\ln\eta/d(1/T)=E_\eta/R$ respectively, where λ is specific conductivity, η

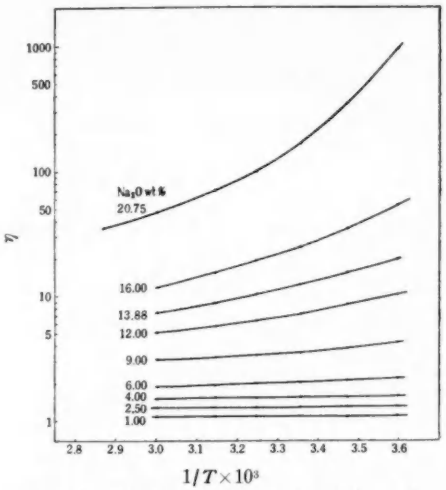


Fig. 3. Variation of the logarithm of viscosity with reciprocal of absolute temperature for the 1.00 molar ratio solutions.

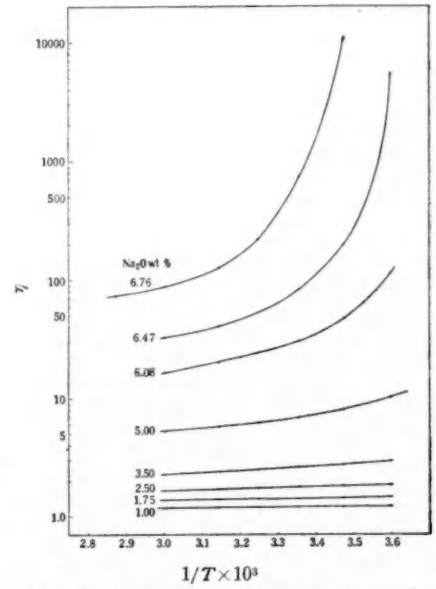


Fig. 4. Variation of the logarithm of viscosity with reciprocal of absolute temperature for the 3.95 molar ratio solutions.

viscosity, T absolute temperature, R gas constant, and E_λ and E_η activation energy of conductance and viscous flow. Their values at 25°C were calculated by the following equation, using those at 15°C and 35°C for λ_1, η_1, T_1 and λ_2, η_2, T_2 respectively.

3) Log $\eta-1/T$ curves for the highly concentrated solutions may no more be postulated as showing linearity. There must be appreciable change of structure with temperature, which results in the marked variation of E_η with temperature.

$$\frac{R(\ln\lambda_2-\ln\lambda_1)}{(1/T_1-/1T_2)}=E_\lambda,\qquad \frac{R(\ln\eta_1-\ln\eta_2)}{(1/T_1-1/T_2)}=E_\eta.$$

In Fig. 5 and 6, the results were plotted against the concentration for all systems studied. It is visualized that for the higher molar ratio solutions the increase of E_λ with concentration is small over an entire concentration range measured, while that of E_η appeared to become remarkably large at high concentration, and that for the lower molar ratio solutions both E_λ and E_η increase with similar manner up to the value several times as large as those in dilute concentration. For the convenience of discussion, the data of E_λ and E_η for the solutions of molar ratio 1.00 and 3.95, as extreme examples, are tabulated in Table I. It seems at first sight rather curious that for the 1.00 molar ratio solution E_λ is smaller than E_η even at dilute concentration range. This may be ascribed to the OH ion contribution to the conductivity as described in the previous report. Conductance by OH ion in aqueous solution requires much smaller activation energy (3.4 kcal.) as compared with usual ionic conductance owing to its special conduction mechanism, which is successfully accounted for as a prototropic process where the proton is transferred from a water molecule to an hydroxyl ion.

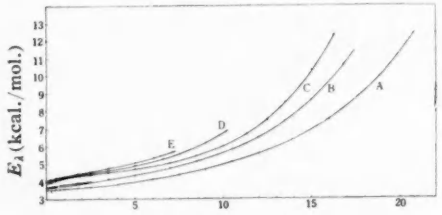


Fig. 5. Variation of the activation energy of conductance with concentration for the sodium silicate solutions of molar ratio.
A: 1.00, B: 1.55, C: 2.13, D: 3.19 and E: 3.95

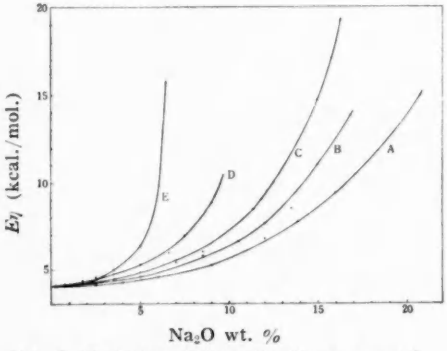


Fig. 6. Variation of the activation energy of viscous flow with concentration for the sodium silicate solutions of molar ratio.
A: 1.00, B: 1.55, C: 2.13, D: 3.19 and E: 3.95

TABLE I

M. R. = 1.00			M. R. = 3.95		
C (Mol./l.)	E_λ	E_η	C (Mol./l.)	E_λ	E_η
0.08	3.52	4.04	0.08	4.14	4.11
0.16	3.57	4.13	0.16	4.23	4.11
0.42	3.69	4.11	0.30	4.40	4.28
0.69	3.84	4.25	0.44	4.54	4.40
1.09	4.11	4.56	0.64	4.74	4.97
1.74	4.68	5.20	0.98	5.04	6.31
2.47	5.54	6.70	1.25	5.32	9.78
2.97	6.31	7.67	1.35	5.43	15.61
3.58	7.48	9.37	1.44	5.55	179.8
5.15	12.37	14.90	1.53	5.64	

The Product of Equivalent Conductivity and Solution Viscosity.—According to Eyring[4], activation free energy of viscous flow ΔF_η is expressed as

$$\eta=hN/V\exp(\Delta F_\eta/RT) \qquad (1)$$

while equivalent conductivity Λ, as a result of theoretical treatment of rate process, may be expressed in terms of activation free energy of conductance ΔF_λ as follows[5],

$$\Lambda=\frac{V^{2/3}\Sigma Z_iF^2\cdot10^7}{hN}\exp(-\Delta F_\Lambda/RT) \qquad (2)$$

where h denotes Planck's constant, N Avogadro number, V molal volume of moving unit, F the Faraday, and z charge valence.

If approximation can be made that the ΔF_η has the same value as ΔF_Λ and that volume of moving unit is similar in both cases the product $\Lambda\eta$ becomes

$$\Lambda\eta=\Sigma z_iF^2\cdot10^7/V^{1/3} \qquad (3)$$

Equation (3) implies that $\Lambda\eta$ is constant irrespective of variation of temperature and concentration, if the viscous flow and electric conduction occur by the same mechanism, and the volume of the moving unit is alike in both cases, and that its value should be the order of unity. Though this relationship has been derived only by the formal treatment of the theory of rate process basing on drastic assumption, it would be interesting to see how it can be applied for the sodium silicate solution. Fig. 7 exhibits the dependence of $\Lambda\eta$ on concentration, again for the molar ratio 1.00 and 3.95 solutions. The figure

4) S. Glasstone, K. J. Laidler and H. Eyring, "The theory of rate process", McGraw-Hill Book Co., New York, N. Y., 1941, First Edition.

5) This formula was derived for a single ion as follows, $\Lambda=uF$, u is a mobility of ion under unit potential and related to diffusion coefficient D_i as $u=D_ize/kT$. Then $\Lambda=D_iz^2F^2/RT$. From the reaction rate theory $D_i=\kappa\cdot V^{2/3}/N$, where κ is the specific rate constant, expressed as $\kappa=kT/h\exp(-\Delta F/RT)$, hence, Λ is given as

$$\Lambda=V^{2/3}z\cdot F^2\times10^7/h\exp(-\Delta F/RT)$$

Therefore, strictly, D_i should be the sum of that for each component ion, and herein the sum of averages was taken.

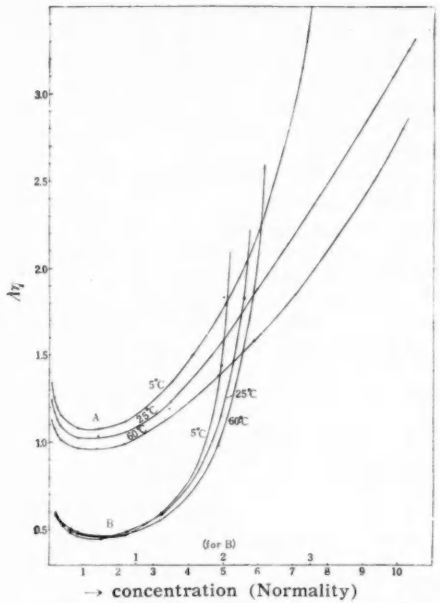


Fig. 7. Variation of the product of equivalent conductivity and viscosity with concentration for the sodium silicate solutions of molar ratio.
A: 1.00 B: 3.95

shows that $\Lambda\eta$ decreases a little in dilute concentration region and becomes constant over a certain range, then begins to increase above the value marked at start point up to a remarkably large one. The initial decreasing part of $\Lambda\eta$ curves is thought to have been brought about by the increase in molal volume with concentration as expected from the equation (3). Also, the smaller value of $\Lambda\eta$ for the high molar ratio solution may well be ascribed to the larger molal volume of the solution, as compared with the lower molar ratio ones, while the increase in $\Lambda\eta$ with concentration which takes place above a certain concentration, would predict that the change in activation free energy with concentration become different between conductance and viscous flow. All these trends seem quite similar to those found with simple strong electrolytes[6] except the fact that the degree of rise in $\Lambda\eta$ with concentration approaches a much larger value than the degree for those solutions. It is noticeable, however, that within the moderate concentration range the value of $\Lambda\eta$ spreads for all the systems only in narrow range, viz. between about 0.5 and 1.0, thus well satisfying the requirement of equation (3). As for the variation of $\Lambda\eta$ with temperature, that of the higher molar ratio solution seems independent of temperature as expected from the equation (3) except at higher concentration range. That $\Lambda\eta$ for the 1.00 molar ratio solution decreases with temperature even at low concentration range can be well attributed to the effect of OH ion, $\Lambda\eta$ of which, as stated in the previous paper, decreases with temperature rise even at infinite dilution.

Thus it may be understood that as a whole, the tendency of curves in Fig. 7 shows no speciality which distinguishes them from those for the simple electrolyte solutions. Merely the concentration above which $\Lambda\eta$ begins to increase markedly lies in lower range than with those solutions. From the comparative study on Fig. 5, 6, and Table I it is found that the concentration, where $E\eta$ exceeds E_λ is almost the same as the above-mentioned concentration read in Fig. 7. They were about 1.45, 1.05 and 0.95 N for the solutions of molar ratio 2.13, 3.19 and 3.95 respectively. The value for the last one may be favorably compared with 0.8–0.9 N, above which the equivalent conductivities theoretically computed no longer agree with those observed experimentally and tend to fall increasingly below the latter. For the lower molar ratio solutions two curves in Fig. 5 and 6 never cross, and the similar curves to that in Fig. 7 indicate that the concerned concentration for molar ratio 1.00 and 1.55 are about 2.15 and 1.85 N respectively. It is interesting to compare these values with 5 to 6 N for $NaClO_4$, NaSCN, and NaI, which were recently reported by Miller.

Discussion

The Structure of Concentrated Sodium Silicate Solutions as Interpreted by the Mechanisms of Conductance and Viscous Flow.—The foregoing results revealed that the mechanisms of conductance and viscous flow become different above a definite concentration range for all the systems studied. Herein, discussion has been made as to the actual behavior of the solutions in this concentration region.

Despite the theoretical incompleteness, it is widely accepted that the concentrated electrolyte solutions may be closely modeled after molten salts in view of the fact that they retain short range local order in component distribution, taking quasi-crystalline structure, where anion is most likely considered to play the predominant roll, due to its superiority in ion size to cation. In such a state, cation takes over progressively of the conduction. Thus, the flow of solution begins to be disturbed more and more by anion arrangement, consequently to need larger activation energy, while conductance is still performed in increasing proportion by cation so that its activation energy does not vary very much. Since the silicate ions, as already reported, are much larger than the sodium ion, particularly in the

6) M. L. Miller, *J. Phys. Chem.*, **60**, 186 (1956).

high molar ratio solutions, it would be quite reasonable to expect that this quasi-crystalline structure may be established even at lower concentration with a greater degree, as compared with simple strong electrolyte solutions. Then, with the higher molar ratio sodium silicate solution, as concentration increases above a certain limit, one silicate ion begins to get contact with another so as either to get combined by hydrogen bond or mechanically tangled, thus leading to the establishment of even rigid structure due to a kind of net work at comparatively low concentration, such as to allow the sodium ion to pass freely through its meshes. This situation is best represented in the 3.95 molar ratio solution which has at 2.88 N viscosity of 650 c.p., E_η of 180 kcal., and yet E_λ of only 5.5 kcal., and at 3.07 N E_λ of 5.64 kcal. and viscosity more than 10,000 c.p.. On the other hand, a lower molar ratio solution contains rather small silicate ions together with considerable amount of OH ions, therefore it cannot afford to form net work structure, thus the rigid state as seen in the higher molar ratio one may not be yielded even at strikingly high concentration where solutions are packed so closely that sodium ion itself can no longer move with ease. Hence, E_λ reaches much larger values than with the high molar ratio solutions, while increase of E_η is not so great as with these ones, being parallel with that of E_λ over a wide concentration range. For the comparison of the behavior of various molar ratio solutions, in Fig. 8, the viscosity of solutions at a concentration where maximum specific conductivity was shown, and in Fig. 9, the equivalent conductivity together with E_λ at a concentration where the solutions exhibit the same viscosity, were plotted against the molar ratio. It is recognized that the higher molar ratio solutions have the greater equivalent conductivity than with the lower molar ratio ones if compared on the same level of high viscosity.

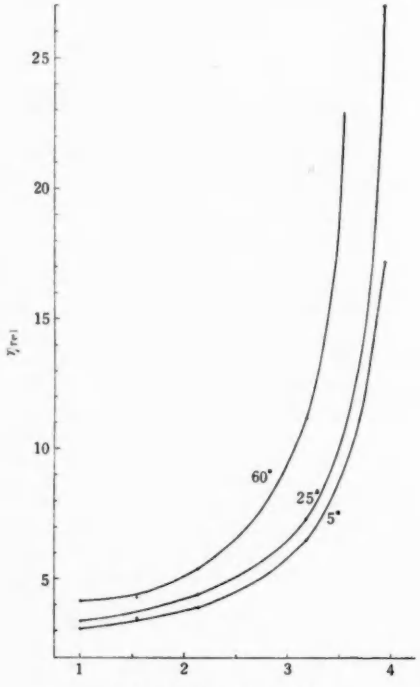


Fig. 8. Viscosity change with molar ratio of sodium silicate solutions at the concentration where maximum specific conductivity is given.

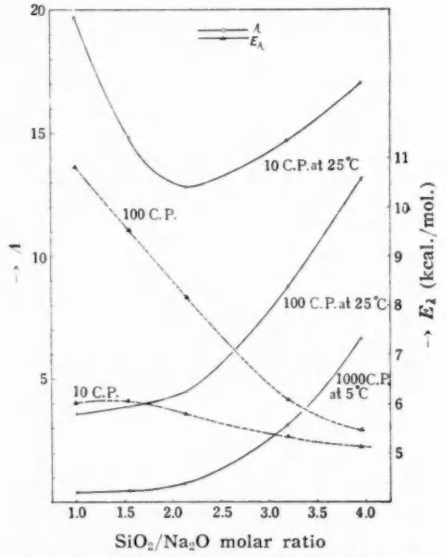


Fig. 9. Iso-viscosity curves 1. Equivalent conductivity 2. Activation energy of conductance—molar ratio relationships.

It would be worth while to estimate the average interionic distance at the highest concentration measured of the molar ratio 1.00 and 3.95 solutions. Assuming the existence of three mole ions in one mole solution, they are calculated as 4.75 Å and 7.11 Å for 10.3 N of the 1.00 molar ratio solution and 3.07 N of the 3.95 molar ratio one.

When the values computed previously of the diameter of corresponding silicate ion, i.e., 7.2 Å and 9.2 Å, are subtracted from the values of three times the foregoing data, there remain 7 Å and 12 Å for two sodium ions in respective solutions. Since the diameter of hydrated sodium ion is supposed to be about 2.5 Å–3.0 Å it is seen that little space is left for the free passage of sodium ion in the former solution, whilst there are still available spaces for the movement of sodium ion in the latter solution. Further, this condition may well be understood if the E_λ of the concentrated sodium silicate solution is compared with those observed for the molten alkali silicates the latter being 10–11 kcal. for all the liquid of silica-alkali weight ratio of 1.5–3.0, according to O'M Bockris et al.[7]. This value of E_λ for molten silicates is much larger than 5.64 kcal. for the 3.95 molar ratio solution at 3.08 N, but lower than 12.4 kcal. for the 1.00 molar ratio one at 10.3 N. Considering these figures and the fact that E_λ is about 5 kcal. for the simple strong electrolyte solutions at 10 N, water in the highly concentrated solution of lower molar ratio seems no longer to be regarded as the solvent but only as a part of kinetic entity as hydration sheath, whereas it is still available as a solvent for the higher molar ratio solution at high concentration, such as to form rigid structure.

The Application of Absolute Reaction Rate Theory to the Conductance of the Concentrated Sodium Silicate Solutions of Molar Ratio 3.95—Now that it seems reasonable to presume that only sodium ion carries electricity under an electric field in the concentrated sodium silicate solutions of high molar ratio, the calculation was attempted in the following of the energy barrier, namely, activation free energy of conductance ΔF_λ on the basis of the absolute reaction theory. Since it is impossible to calculate the height of the energy barrier by means of quantum mechanics in such a complicated system, this height was determined from the experimental conductivity according to the method employed by Eyring in case of the proton transfer in aqueous solution.

When a field having an effective potential gradient Φ is applied, the specific reaction rate at an angle θ to the direction of the field is given by $\kappa = kT/h \exp[-(\Delta F - \delta F)/RT]$ where δF is defined by $\delta F = \Phi \cos\theta \times d \times 23060$, d being half the distance between the initial and the final state along the reaction coordinate. Since the distance travelled by an ion in the direction of the applied field is $2d\cos\theta$, the velocity of an ion in cm/sec, v, is:

$$v = 2d \cdot \cos\theta \cdot kT/h \cdot \exp(-\Delta F/RT) \cdot \exp(a \cdot \cos\theta)$$

where $a \equiv \Phi \cdot d \times 23060/RT$.

This equation applies to motion in one direction only and to obtain the distance moved in the direction of the field it is necessary to take the average over all angles,

$$v = 2d\,kT/h \exp(-\Delta F/RT) \times \frac{\int_0^\pi \exp(a \cdot \cos\theta) \cdot \cos\theta \cdot \sin\theta \cdot d\theta}{\int_0^\pi \sin\theta \cdot d\theta}$$

as the quantity a is very small, so that it is possible to write $\exp(a \cdot \cos\theta) = 1 + a \cdot \cos\theta$, and hence

$$v = 2d \cdot kT/h \cdot \exp(-\Delta F/RT) \cdot a/3.$$

As $\Lambda = vF$ then

$$\Lambda = 2/3 \cdot dF \cdot a \cdot kT/h \cdot \exp(-\Delta F/RT). \quad (4)$$

The effective potential gradient in the liquid Φ has been suggested to be placed equal to $(\varepsilon+2)/3$ for an applied potential gradient of 1 V/cm, where ε is the dielectric constant of the solution. Difficulty arises, however, in knowing the dielectric constant of the solution. Hasted, Ritson and Collie[8] derived for this the equation $\varepsilon = \varepsilon_w + 2\bar{\delta}C$, where ε_w is the dielectric constant of solvent water, $\bar{\delta}$ half the molar depression of dielectric constant of water by electrolyte. This linear relationship is said to hold up to 2 N concentration. Though no data are available for the silicate ion, ε was calculated using this equation with the assumption that $\bar{\delta} = 10$ for sodium silicate, a comparable value to those for NaOH and Na_2SO_4, considering the extent of hydration. As to $2d$, i.e. the distance travelled by an ion in the conduction process in overcoming one potential energy barrier, it may be taken either as the average dimensions of water molecule or as that of SiO_4 tetrahydra, the former being 3.1 Å, the latter 3.2 Å. Therefore $d = 1.6$ Å was used reasonably. The equation (4), then, is expressed as:

$$\Lambda = 3.98 \times 10^3 \times \exp(-\Delta F/RT) = 3.98 \times 10^3 \times \exp(-\Delta H/RT)\exp(T\Delta S/R)$$

7) J. O'M. Bockris, J. A. Kitchener, S. Ignatowitcz and J. M. Tomlinson, *Trans. Farad. Soc.*, **48**, 75 (1952).

8) J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

TABLE II

C (Mol./l.)	Λ	ΔF (kcal.)	ΔH (kcal.)	ΔS (e.u.)	η	ΔF_η (kcal.)	ΔH_η (kcal.)	ΔS_η (e.u.)
1.53	11.64	5.12	5.70	1.9				
1.44	12.72	5.09	5.59	1.7	650.1	6.17	179.8	583
1.35	13.60	5.07	5.53	1.5	74.11	4.88	15.61	36.0
1.25	14.81	5.04	5.38	1.1	27.52	4.29	9.78	18.4
0.983					6.22	3.40	6.31	9.77
0.646					2.36	2.80	4.97	7.28
0.443					1.60	2.56	4.40	6.19

ΔH is heat of activation and may be taken approximately as equal to the experimental activation energy E_Λ[9], and ΔS the activation entropy. In table II the results of calculation for ΔF and ΔS are shown along with the experimentally observed Λ and ΔH for the 3.95 molar ratio solution at several high concentrations. Also the same terms for viscous flow were computed from the equation (1), using the average molar volume over all the solute ions and solvent one, as V.

It is visualized that the activation free energy of conduction is almost the same as the activation energy which was obtained experimentally; that is, the entropy in the activated state is only slightly larger than in the equilibrium state, while the activation entropy of viscous flow increases rapidly with concentration. This implies that in order to cause the viscous flow some short range local order should be broken down; on the other hand, for the conduction process it is scarcely necessary to disrupt this structural order. Thus, the entropy behavior may be interpreted as the evidence of the occurrence of this local order which does not disturb the passage of sodium ion under electric field. Consequently this confirms the foregoing discussion.

Conclusion

The activation energies of conductance and viscous flow, E_λ and E_η, were computed from the experimental results of temperature dependence of conductivity and viscosity for the sodium silicate solutions of various molar ratio. And it was found that as concentration increases above a definite range, E_η becomes progressively larger than E_λ, to the greater extent with the higher molar ratio solutions, and that the product of equivalent conductivity and viscosity may be regarded almost as independent of concentration and temperature below a definite concentration range, above which it increases rapidly. This critical concentration range for the 3.95 molar ratio solution approximately coincides with that, below which the equivalent conductivities theoretically computed agree with those experimentally observed.

These results were considered to show that in the concentrated sodium silicate solutions, short range local order comes to be established so as to make a quasi-crystalline structure in which silicate ions take a predominant role. This tendency is greater for the higher molar ratio solution, where the arrangement of silicate ions proceeds until it yields even rigid net work structure, while sodium ion can still freely pass through the meshes.

Assuming this model for the concentrated sodium silicate solution of molar ratio 3.95, the activation free energy and entropy were calculated from the conductivity at high concentration region, using the absolute reaction rate theory. The results also confirmed the above interpretation.

Thus, it may be concluded that the electric conductance behavior of the sodium silicate solutions could be explained by regarding them as a kind of strong electrolyte solution over an entire range of concentraion, since within the moderate concentration range the conductivity could be theoretically accounted for, and even at the higher concentration, as described above its behavior would not be different essentially from those seen with simple strong electrolyte solutions, if the difference of anion size and extent of hydration is considered.

The author wishes to express his sincere thanks to Dr. Tadashi Yawataya for his kind support throughout this work.

Research Laboratory Asahi Glass Co. Ltd. Tsurumi, Yokohama

9) E_Λ may be related to E_λ as follows, since $\Lambda=1000/(w\rho/M)$, where w is weight of solute per 1000 g solution, ρ density of solution, M molecular weight of solute. Then, $d\ln\Lambda/d(1/T)=d\ln\lambda/d(1/T)-d\ln\rho/d(1/T)$, $-E_\Lambda/R=-E_\lambda/R+T^2/\rho\cdot d\rho/dT$. If ρ is expressed as $\rho=\rho_0[1+\alpha(T-T_0)]^{-1}$, then, $E_\Lambda=E_\lambda+RT^2[1-\alpha(T-T_0)]$. As α is the order of 0.01%, the difference between E_Λ and E_λ is not large.

*Effect of the Addition of Some Carbohydrates on the Decomposition Rate of Sodium Aluminate Solutions with Seeding**

By Taichi SATO

(Received December 26, 1956)

Introduction

The Bayer process is today the most widely used method for the production of alumina. Of this process it is usually said that the precipitation of crystalline aluminum hydroxide from a sodium aluminate solution is actually performed in the presence of organic matter[1-3]. When alumina hydrate in bauxite is dissolved with a solution of caustic soda, some organic matter found in bauxite such as humus etc. dissolves too and accumulates in the alkali solution. Two methods have been proposed to avoid this phenomenon. The first is the destruction of organic matter by a calcination of bauxite at temperatures from 350° to 400°C before grinding. The second is the separation of organic matter by concentrating an alkali solution after the precipitation cycle.

Recently, however, the calcination of bauxite before grinding is not carried out in most of the alumina plants. The omission of this calcination is a debatable problem. At present, we can not answer whether this calcination will be necessary or not. From an industrial view point, the effect of the presence of organic matter on the precipitation of aluminum hydroxide from a sodium aluminate solution has an important meaning as it relates to the problem of the necessity of calcination. On the other hand this study will, beside being an academic problem, give us interesting results with regard to crystal growth and to reaction between inorganic compound, organic matter, etc. But the reports on this problem are few till now, because the phenomenon in which the presence of organic matter has influence on the precipitation of aluminum hydroxide from a sodium aluminate solution is a complicated one. Therefore this study was undertaken as the continuation of the writer's former studies[4], and it has the object of investigating fundamentally the influence of the presence of organic matter on the decomposition of sodium aluminate solution. As the first step, the investigation on the decomposition rate of sodium aluminate solution with seeding and some carbohydrates has been made.

Experimental Methods

Various amounts (0.1, 0.3, 0.5, 1, 3, 5, 10 and 20 g./l.)*1 of glucose, sugar and starch as the representatives of carbohydrate were added to sodium aluminate solution (NaOH 140.0 g./l., Al_2O_3 105.0 g./l., mol. ratio $Na_2O/Al_2O_3=1.7$). These solutions were decomposed with seeding of hydrargillite*2 (5 or 10 %*3) at a temperature of 30°C, and those decomposition rates were measured. Here the decomposition rate is given by a change of decomposition ratio expressed as follows;

$$\frac{x_1-x_2}{x_1}\times 100(\%)$$

where x_1 and x_2 are the concentrations of alumina contained in sodium alminate solutions before and after decomposition.

The carbohydrates used were as follows. Glucose of dehydrated reagent class, and cane sugar was purified by a reprecipitation of ordinary sugar obtained in the market. Starch was made by refining white potato. The contained moistures were measured with Abderhalden's drying apparatus*4. The obtained values were as follows; 0.26 % in glucose, 1.25 % in sugar and

* This paper is written as the 16th report of Studies on the Hydrolysis of Sodium Aluminate Solutions.

A partial report was made at the Autumn Meeting of Kanto Subgroup of the Chemical Society of Japan, held in Tokyo on November 6th, 1955.

1) "Gmelins Handbuch der anorganischen Chemie", Nr. **35**,Al[B], (1933), S. 34.

2) J. D. Edwards, F. C. Frary and Z. Jeffries, "Aluminum Industry, Aluminum and its Production", Mc. Graw-Hill, New York (1930), p. 128, 160.

3) F. Ullmann, "Enzyklopädie der technischen Chemie", Bd. I, (1928), S. 306.

*1 These values designate net weight of carbohydrate exclusive of moisture.

4) T. Sato, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **54**, 266, 755 (1951); **55**, 66, 198 (1952); **56**, 399, 478, 743, 840 (1953); **57**, 20 111, 355, 540, 805 (1954); **58**, 325, 556 (1955).

*2 This was previously precipitated by decomposition with seeding of sodium aluminate solution of NaOH 140.0 g./l., Al_2O_3 105.0 g./l., mol. ratio $Na_2O/Al_2O_3=1.7$ at 30° C.

*3 This is a percentage to the amount of alumina contained in sodium aluminate solution.

*4 Aceton was used.

18.47 % in starch. These substances were added to sodium aluminate solution in the dry state.

The method of decomposition of sodium aluminate solution with seeding is as follows[5]. Sodium aluminate solution was prepared by the dissolution of aluminum (99.85 %) into a solution of caustic soda (NaOH 140.0 g./l.). 250 cc. of the solution was put in a wide-mouthed bottle of 500 cc. capacity and it was agitated with a seed charge of the prepared hydrargillite in a constant temperature water bath. The amount of alumina contained in sodium aluminate solution was determined gravimetrically.

As the viscosity of sodium aluminate solution may be influenced by the swelling of added starch particles, it was measured with Ostwald's viscosimeter at a temperature of 30°C. In this case its viscosity has to be measured after the attainment of swelling-equilibrium of starch particle. Therefore, at first, the swelling behavior of starch was investigated, and then the time within which the starch particle will attain the swelling-equilibrium was determined. Namely 1 g./l. of starch added to the caustic soda solution of prescribed concentration (NaOH 140.0 g./l.) was swollen under agitation at a temperature of 30°C. the same as in the case of decomposition with seeding of sodium aluminate solution, and the viscosity of its solution was measured after some prescribed times. Next, the sodium aluminate solutions containing 1, 3, 5 and 10 g./l. of carbohydrates were left for a prescribed time*5, and then these amounts of viscosity were measured.

The Effect of the Addition of Carbohydrate on the Decomposition Rate

The decomposition rates, with seeding of 5 % hydrargillite, of sodium aluminate solutions containing glucose, sugar and starch are given in

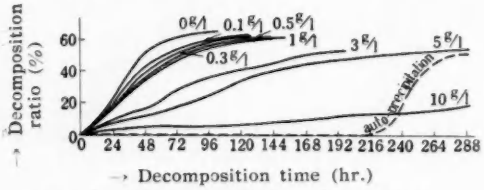


Fig. 1. Effect of addition of glucose on decomposition rate with 5% seeding.

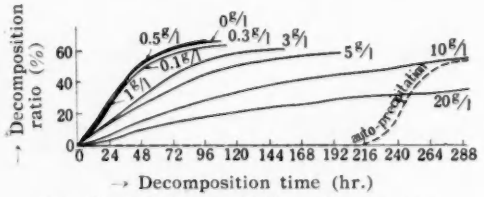


Fig. 2. Effect of addition of sugar on decomposition rate with 5 % seeding.

5) T. Sato, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **58**, 325 (1955).

*5 This time is six hours in Fig. 8.

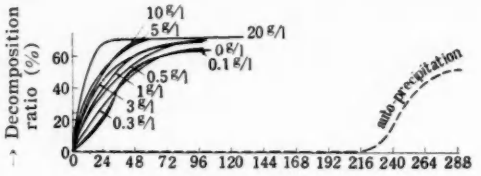


Fig. 3. Effect of addition of starch on decomposition rate with 5 % seeding.

Figs. 1, 2 and 3. Furthermore the decomposition curve of auto-precipitation is shown in these Figs.

Fig. 1 shows that the addition of glucose gives a retarding action on the decomposition with seeding, and that its action grows with the increase of the added amount. Thereafter the decomposition rate with the addition of 10g. glucose/l. is much smaller than in the case of auto-precipitation. Fig. 2 shows that the addition of sugar retards the decomposition of sodium aluminate solution as in the case of the addition of glucose. In this case we observe the tendency that the decomposition is retarded with the increase of the added amount but with the exception of the addition of 0.3, 0.5 and 1 g. sugar/l. As the addition of 0.3, 0.5 and 1 g. sugar/l. are considered the same, with no addition in the decomposition curves, the addition of 0.1 g. sugar/l. will have no influence on the decomposition. Though the tendency of Fig. 3 is different from those of Fig. 1 or 2, yet Fig. 3 suggests that the addition of starch promotes the decomposition. The decomposition is not promoted with the addition of 0.1 g. starch/l., but it begins to be promoted with the addition of 0.3 g. starch/l. Then the decomposition rate is rapidly improved with the addition of more than 0.5 g. starch/l. However, on the addition of starch to sodium aluminate solution its viscosity becomes as large as Fig. 9 indicates.

In order to investigate the actions on the decomposition of glucose, sugar and starch in all of the results of Figs. 1, 2 and 3, the comparison of decomposition rate with the addition of 1, 5 and 10 g./l, for example, is made in Fig. 4.

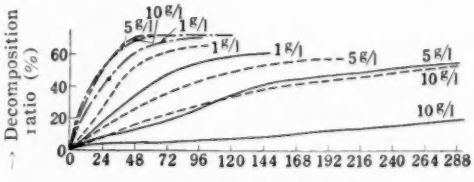
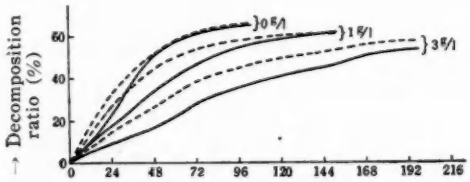


Fig. 4. Comparison of decomposition rate with 5 % seeding in presence of 1, 5 and 10 g./l. of glucose, sugar and starch respectively.
glucose
- - - - sugar
— - — starch

Fig. 4 shows that the retarding action of glucose is obviously larger than that of sugar. In Fig. 4 the decomposition rate with the addition of 5 g. glucose/l. coincides with those of the addition of 10 g. sugar/l. Such a result may be due to the difference in molecular formulas ($C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$) of glucose and sugar. Because the numbers of molecules of glucose contained in the same weight are about twice the number in the case of sugar.

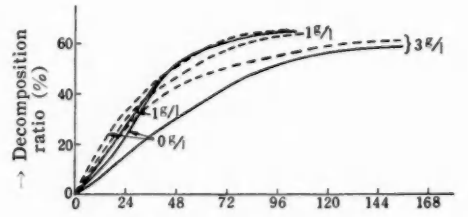
Relation between the Amount of Seed and the Addition of Carbohydrate

As Figs. 1, 2, 3 and 4 are given with 5% seeding, the decomposition rate was next investigated with 10% seeding. Then the comparison of decomposition rate between 5 and 10% seeding was made with the addition of carbohydrate. In this experiment the added amounts of carbohydrates were 1 and 3 g./l. in the case of glucose or sugar, and 0.5, 1, 3 and 5 g./l. in starch. These results are given in Figs. 5, 6 and 7.



→ Decomposition time (hr.)

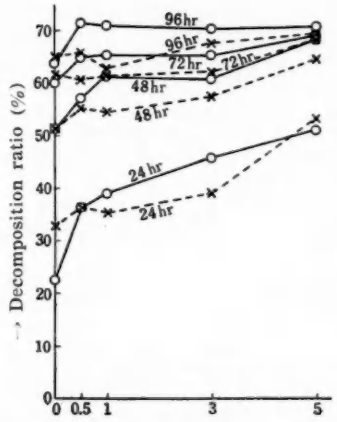
Fig. 5. Relation between amount of seed and addition of glucose.
—— 5% seeding
- - - 10% seeding



→ Decomposition time (hr.)

Fig. 6. Relation between amount of seed and addition of sugar.
—— 5% seeding
- - - 10% seeding

Fig. 5 shows that the decomposition rate with 10% seeding is larger than that of 5% seeding by the addition of glucose. This result suggests that the presence of seed charge acts stronger on the decomposition than glucose does. Fig. 6 shows that though with an exception of addition of 1 g. sugar/l., the decomposition rate with much seeding is larger than that with a little seeding on the addition of sugar the same as in the case of glucose. On the addition of starch



→ Added amount of starch (g./l.)

Fig. 7. Relation between amount of seed and addition of starch.
○ 5% seeding
× 10% seeding

as shown in Fig. 7, 10% seeding promotes the decomposition the same as 5% seeding, but its effect is smaller than the effect of 5% seeding.

Discussion

From the above-mentioned results it is obviously seen that the addition of glucose or sugar retards the decomposition of sodium aluminate solution, and that the addition of starch promotes its decomposition. But the viscosity of sodium aluminate solution is improved with the addition of starch. Hence the viscosity of sodium aluminate solution containing carbohydrate was measured in order to investigate the effect of the viscosity of solution on the decomposition. On the addition of starch to sodium aluminate solution, as starch particle is steadily swollen by alkali, the viscosity of the solution in the swelling-equilibrium of starch is different from that which occurs before swelling. W. Ostwald and G. Frenkel[6] reported that the swelling of starch by alkali had taken a long time to attain the equilibrium. C. E. Mangels and C. H. Bailey[7] measured the viscosity of the solution left for three hours after the addition of alkali to starch particle, and H. Suzuki and N. Taketomi[8] measured the viscosity of solution left for from five to ten minutes after the addition of alkali. In these studies, however, the concentration of alkali solutions are below 1 N, and they are not so high as this study treats. Hence the viscosity of sodium

hydroxide solution (NaOH 140.0g./l.) with the addition of 1 g.starch/l. has been measured in order to investigate the swelling behavior of starch. This result is given in Fig. 8.

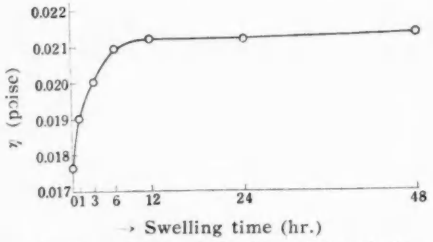


Fig. 8. Swelling behavior of starch in sodium hydroxide solution at 30°C. (1 g./l. of starch in NaOH 140.0 g./l.)

Fig. 8 shows that the starch particle may attain the equilibrium of swelling within about from six to twelve hours. Therefore the viscosity of sodium aluminate solutions with the addition of carbohydrates have been measured, six hours after their addition to the solution. These results are contained in Fig. 9.

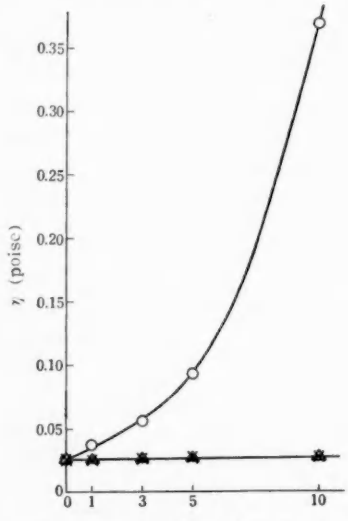


Fig. 9. Changes of viscosity of sodium aluminate solutions in presence of glucose, sugar and starch at 30°C.
△ glucose
× sugar
○ starch

Fig. 9 shows that the viscosity of sodium aluminate solution is not improved with the increase in an added amount of glucose or sugar, and that it is very much influenced by the addition of starch. However the viscosity of sodium aluminate solution with added starch may be improved by the swelling of starch at first, and then it may be rapidly lowered with the hydrolysis of starch initiated by the action of alkali, because the concentration of alkali is high. Though the viscosity of solution is almost unchanged after the swelling as shown in Fig. 8, then starch will not be influenced by alkali for the period of decomposition with seeding in this study. These results suggest the viscosity of solution is not a factor of first order for the decomposition.

On the one hand, from the results of decomposition rate, the action of starch on the decomposition is obviously different from that of glucose or sugar. Hence, the writer thinks, glucose or sugar (or their oxidation products by alkali in solution) binds with Al^{3+} or $Al(OH)_3$ molecules, and they must be soluble in solution forming some compounds (for example such as saccharate). R. K. Gupta and H. E. Buckley[9] who investigated the effect of the presence of dye on the solubility of a solution considered a binding of dye and solute. The writer believes this idea may be applied to this study too. However, if the phenomena in this study should be discussed only by Gupta's thought, this decomposition has to give us such an induction period as auto-precipitation[10], because the addition of glucose or sugar makes lower the degree of supersaturation of alumina to caustic soda in solution. Auto-precipitation has an induction period and is rapidly promoted after passing that period. On the other hand, the seeding decomposition with the addition of glucose or sugar has not an induction period, and it progresses very slowly. This shows obviously the difference of decomposition mechanism between auto-precipitation and seeding decomposition with the addition of carbohydrate. In auto-precipitation, crystal nuclei are gradually formed in an induction period, and then the formation of these certain definite numbers promotes

6) W. Ostwald and G. Frenkel, *Kolloid-Z.*, **43**, 296 (1927).
7) C. E. Mangels and C. H. Bailey, *J. Am. Chem. Soc.*, **55**, 1981 (1933).
8) H. Suzuki and N. Taketomi, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **59**, 45 (1956).
9) R. K. Gupta and H. E. Buckley, *Z. physik. Chem.*, **204**, 165, 175 (1955).
10) T. Sato, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **54**, 755 (1951).

rapidly the precipitation of aluminum hydroxide. On the addition of glucose or sugar these bind with solutes in solution, and the degree of supersaturation of alumina to caustic soda becomes lower. Further, in this case, the activity of seed is decreased by a binding of seed charge and these carbohydrates. Therefore it seems that the formation of new crystal nuclei is retarded on the seeding decomposition with the addition of glucose or sugar. But it is obviously seen from the decomposition curves of Figs. 5 and 6 that the binding of glucose or sugar with solute is weak. In the meanwhile, it is observed from Fig. 4 that the binding between glucose and solute is stronger than that of the binding between sugar and solute.

On the other hand, the action of starch on the decomposition will be considered in relation to the facts[11] that starch is added in order to promote the separation of red mud from sodium aluminate solution. The starch added to the solution will bind with seed charge at first. E. Herrmann and others[12,13] who studied the separation of red mud in the sodium aluminate solution with the addition of starch as one of the colloid-chemical problems, pointed out that the addition of 0.25 g. starch/l. gives the optimum aggregation to red mud, and that at high starch concentration starch acts as a protective colloid for individual particles. Therefore, in this study too, more or less amounts of added starch will have a great influence on the agglomeration of particles. As the starch particle is apt to suffer hydration, it is chemisorped by OH^- on the surface of seed and it causes the aggregating phenomena of individual particles by the bridge action towards other particles. When starch particles chemisorped on the surface of seed are increased, these act as a protective colloid for individual particles and disturb the aggregation of particles. However, as the active surface of seed is diminished by the absorption of starch on its surface, the decomposition with seeding of sodium aluminate solution is retarded, and the effects on the decomposition grow remarkably with the increase in the added starch. And then the decomposition is evidently promoted with the addition of starch as shown in Figs. 3 and 7. Therefore, in the opinion of the present writer the presence of starch in itself must have a promotive action*6. From the above discussion this writer believes two counter phenomena play an important role in the action of starch on the decomposition rate. First, starch is retarding in the active surface diminished by the chemisorption on the surface of seed-crystallites (negative action). Second, starch is promoting in some way on the decomposition rate (positive action). As mentioned above, Fig. 7 shows that the decomposition rate with 5 % seeding on the addition of starch is larger than that of 10 % seeding. This may owe to aggregating phenomena of seed caused by starch. It seems that the condition of this experiment with 5 % seeding and starch addition has not been necessary (for example, the dispersed concentration of seed in solution) to get the aggregation by starch-bridge. Therefore, as seed charge of 10 % seeding is aggregated by starch more than in the case of 5 % seeding, the surface area of seed under 10% seeding may be diminished by the formation of a big agglomeration of particles.

Moreover the sedimentation behavior of a particle precipitated by the decomposition of sodium aluminate solution with seeding and starch addition has been investigated. Consequently the sedimentation behavior of a particle precipitated with 5 % seeding indicates an aggregated sedimentation (that is, suspension layer settles in forming clearly a boundary from dispersed phase), and that of 10 % seeding points a tendency of free sedimentation (that is, with the state of suspension, dispersed particles settle steadily from a large particle to a small one, and a boundary of suspension layer is not clear). As these results may be closely connected with the action mechanism of starch, the writer intends to investigate these problems in his next report.

In this study the influence of temperature on carbohydrate need not be considered, because the decomposition of sodium aluminate solution has been made at the temperature of 30°C.

Summary

In order to study the influence of the

11) W. Kerr, "Chemistry and Industry of Starch", Academic Press, Inc., New York (1950), p. 645.
12) E. Herrmann, I. Dvornik, O. Korelić and V. Matković, *Kolloid-z.*, **123**, 22 (1951).
13) I. Dvornik and E. Herrmann, ibid., **128**, 75 (1952).

*6 It seems that the effect of starch on the decomposition is owing to amylose or amylopectin. This point will be investigated in a later report.

presence of the organic matter in a sodium aluminate solution the decomposition rate was investigated by the addition of some carbohydrates as first step of study. Three kinds of carbohydrate, i. e. glucose, sugar and starch (white potato) were chosen and added to a sodium aluminate solution in verious amounts. These solutions were decomposed with seeding of hydrargillite, and these decomposition rates were compared in each case. Consequently it had been observed that the addition of glucose or sugar acts to retard the decomposition, and that the increase of an added amount of starch promotes the decomposition. But the retarding action of glucose is larger than that of sugar. On the other hand, the relation between the added amount of seed and the addition of carbohydrate was investigated. It had been seen that the presence of seed is stronger than that of glucose or sugar in the action of decomposition, and that this relation is different upon the presence of starch. Further the viscosity of sodium aluminate solution mixed with carbohydrate was measured. It has been observed from this measurement that the viscosity of sodium aluminate solution is almost unchanged with the addition of glucose or sugar, and that its viscosity is improved with the addition of starch. Then these results have been compared with the decomposition rate. From this result, it is concluded that the viscosity of solution does not always act on the decomposition as the factor of first order. Hence the action mechanism of these carbohydrates on the decomposition are discussed, and it is clearly concluded that there is a very large difference among the actions of each carbohydrate on the decomposition. In these results one must obtain some informations upon the action mechanism on the decomposition of sodium aluminate solution in the presence of organic matter.

The author wishes to express his hearty thanks to Dr. Erich Herrmann of Martinswerk G. m. b. H., Bergheim and Mr. Siniša Maričić of Institute of Physics Zagreb for their very helpful discussion.

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Microcolorimetric Determination of Organic Sulfur by the Tin(II)-Strong Phosphoric Acid Reduction Method

By Toshiyasu KIBA, Ikuko AKAZA, née KISHI and Sachiko TAKI

(Received January 9, 1957)

It has long been desired by organic, biological, and medical chemists that some rapid and accurate methods for the determination of minute amounts of sulfur in organic and biological materials might be developed. The determination of organic sulfur ordinarily consists of two steps, i.e. the oxidation of the sulfur to sulfate and the estimation of the sulfate. However, oxidation of organic sulfur requires time, skill and patience even by the use of an elaborate apparatus and powerful reagents, and, furthermore, reliable estimation of the sulfate is not always easy, whether it is worked out colorimetrically or turbidimetrically. If the oxidation of organic sulfur can be completed under mild conditions with the use of an open vessel, and if the resulting sulfate can be reduced to hydrogen sulfide in some simple way, the determination of the organic sulfur will become easier and more sensitive. Although various oxidizing and reducing procedures have been proposed for this purpose[1-11], they are so

1) R. K. Siegfriedt, J. S. Wiberley and R. W. Moore, *Anal. Chem.*, **23**, 1008 (1951).
2) E. Kahane, *Oster. Chem-Ztg.*, **55**, 209 (1954).
3) E. Kahane and M. Kahane, *Bull. Soc. Chim.*, **1**, 280 (1954).
4) E. Woloensky, *Ind. Eng. Chem.*, **20**, 1234 (1928).
5) G. F. Smith and A. G. Dean, *Ind. Eng. Chem. Anal. Ed.*, **4**, 227 (1932).
6) P. O. Bethge, *Anal. Chem.*, **28**, 119 (1956).
7) I. S. Lorant, *Z. Physiol. Chem.*, **185**, 245 (1929).
8) C. L. Luke, *Ind. Eng. Chem. Anal. Ed.*, **15**, 602 (1943).
9) H. Roth, *Mikrochimie ver. Mikrochim. Acta*, **36-37**, 379 (1951).
10) C. M. Johnson and H. Nishita, *Anal. Chem.*, **24**, 736 (1952).
11) C. M. Johnson and T. H. Arkley, *Anal. Chem.*, **26**, 1525 (1954).

far too complicated to be readily applicable to routine works.

In this laboratory strong phosphoric acid has been used for the last five years for many analytical purposes with excellent results, and in a previous paper[12] the authors reported a new rapid colorimetric method for the determination of minute amounts of sulfate, in which the tin(II)-strong phosphoric acid, a new powerful reducing agent first described by the authors, was used[13]. In the present investigation, this method has been extended to the determination of organic sulfur of the order of micrograms by means of preliminary oxidation of organic sulfur with chromium(VI)-strong phosphoric acid, a new powerful oxidizing agent which is composed of potassium dichromate and strong phosphoric acid[14]. The rapidity and the simplicity of the original method are still retained in this procedure, by which 1 to 35 micrograms of organic sulfur can be estimated colorimetrically.

Apparatus

Apparatus for Oxidation, Reduction and Absorption.

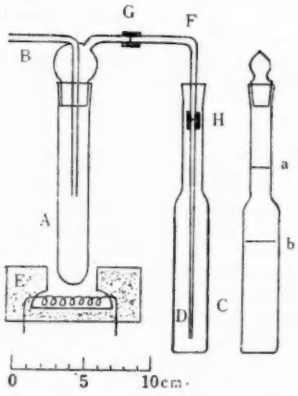

Fig. 1. Apparatus for oxidation, reduction and absorption.
A: Reaction vessel of fused silica
B: Glass cap fitted to a reaction vessel
C: Absorbing vessel
a: The 35 ml. mark
b: The 50 ml. mark
D: Detachable delivery tube (4 mm. in outside diameter)
E: Electric heater
F: Gas leading tube
G, H: A short piece of rubber tubing

12) T. Kiba and I. Kishi, This Bulletin, **30**, 53 (1957).
13) T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, ibid., **28**, 641 (1955).
14) S. Ohashi, ibid., **28**, 645 (1955).

The vessel for the oxidation of organic sulfur to sulfate is a test-tube of fused silica, which can be used also as the reaction vessel for the reduction of the sulfate. The test-tube should be made of fused silica, since unexpectedly high values of sulfur were occasionally obtained when glass vessels were used, owing to minute amounts of sulfur in the glass.

A set-up of the apparatus for the reduction of the sulfate to hydrogen sulfide and the absorption of the hydrogen sulfide evolved is shown in Fig. 1. Six gas-washing bottles (not shown) are placed between a Kipp's apparatus for the production of carbon dioxide and the inlet arm of the reaction vessel (A). Solutions used for the purification of the carbon dioxide are described below. A bent glass tube (F) is attached to the outlet arm of the reaction vessel with a short piece of rubber tubing (G). A detachable delivery tube (D) is connected with another rubber tubing to the bent tube (F) and inserted into the absorbing vessel (C). Since some zinc sulfide adheres to that part of the tube immersed in the solution, it must be disconnected and allowed to remain in the absorbing vessel during the development of the methylene blue color.

Photoelectric Colorimeter.—A "Hirama" photoelectric colorimeter with 1-cm. cells and a filter of 655 mμ was used throughout this work.

Reagents

Tin(II)-Strong Phosphoric Acid.—Prepare from 250 g. of strong phosphoric acid and 50 g. of tin(II) chloride dihydrate of extra pure grade as described in the previous paper[13].

Chromium(VI)-Strong Phosphoric Acid.—Prepare from potassium dichromate and diluted tin(II)-strong phosphoric acid by the following precaution. Even in the case of extra pure grade, potassium dichromate and phosphoric acid always contain minute amounts of sulfate as impurity, which may give occasionally too high values in the determination of sulfur by this method. In the present study, the authors used potassium dichromate of the purest reagent grade supplied by the Osaka Goverment Industrial Research Institute, which contained as little as 0.0015% of sulfate. A commercial reagent should be recrystallized twice from sulfur-free water. Sulfates contained in commercial phosphoric acid could be removed as follows: add 1 g. of tin(II) chloride dihydrate of pure grade into 100 g. of strong phosphoric acid and heat it to 300°C just as in the preparation of tin(II)-strong phosphoric acid. By this treatment, the sulfates contained in the phosphoric acid is removed as hydrogen sulfide during the heating. This will be called "Diluted Tin(II)-Strong Phosphoric Acid" in the following description. In an Erlenmyer flask, dissolve 12g. of potassium dichromate of the purest grade in 100 g. of the diluted tin(II)-strong phosphoric acid by heating on a steam bath. The chromium(VI)-strong phosphoric acid thus prepared can be stocked in a stoppered vessel without dehydrant, but it is advisable to prepare the

reagent soon before use.

Carbon Dioxide.—Purify the carbon dioxide produced in the Kipp's apparatus by passing it through five gas-washing bottles containing, respectively, water, 1% potassium permanganate in 10% sodium carbonate solution, vanadium(II) sulfate in sulfuric acid (see below), 5% barium chloride, and zinc acetate absorbing solution (see below). Place a sixth bottle, an empty one, for the purpose of equalizing the flow and of intercepting floating liquid droplets.

Vanadium(II) Sulfate Solution.—Dissolve 2g. of ammonium vanadate in 200ml. of water, add 20 ml. of 6 N sulfuric acid, and shake vigorously with 3% zinc amalgam in an atmosphere of carbon dioxide until the violet color of vanadium(II) appears. Transfer the solution quickly into a gas-washing bottle containing a small amount of the amalgam. This is employed to remove oxygen completely from the carbon dioxide.

Zinc Acetate Absorbing Solution.—Dissolve 20 g. of zinc acetate dihydrate of extra pure grade in 1 l. of redistilled water. If necessary, add two or three drops of glacial acetic acid to clarify the solution, but the pH of the solution should not be below 5. The redistilled water is prepared by distilling ordinary distilled water with a small amount of sodium hydroxide in an all-glass still.

***p*-Amino Dimethylaniline Solution.**—Dissolve 1.4 g. of *p*-amino dimethylaniline sulfate crystals of pure grade in 200 ml. of 1 : 1 sulfuric acid.

Ferric Chloride Solution.—Dissolve 10 g. of ferric chloride hexahydrate in 100 ml. of distilled water.

Standard Sulfate Solution.—Dissolve 4.4299g. of unhydrous sodium sulfate of extra pure grade in 1 l. of sulfur-free water. Take 20 ml. of this solution with a pipet and dilute it to 1 l. so that the final solution contains 20 micrograms of sulfur in 1 ml. Pipet accurately the required volume of this solution for making the standard calibration curve for the colorimetric determination of sulfur.

Barium Chloride Solution.—Dissolve 1 g. of barium chloride dihydrate in 100 ml. of sulfur-free water, and use 0.5 ml. of the solution in each test.

Procedure

When the sample is a solution, pipet accurately an aliquot containing 1 to 35 micrograms of sulfur. When it is a solid, take an accurately-weighed quantity containing the same range of sulfur. Put the measured sample into the test-tube of fused silica. Add 0.5 ml. of the barium chloride solution and evaporate the contents to dryness at the bottom of the vessel in a water-bath. Pour 1 ml. of the chromium (VI)-strong phosphoric acid over the residue from a pipet. Dip the vessel into a steam-bath till the content appears homogeneous. Place the vessel on an electric heater (E) (Fig. 1) and heat gently for about ten minutes to decompose the organic matter completely. The color change of the content from red to green shows the end of the reaction. Cool the content and pour 5 ml. of the tin(II)-strong phosphoric acid into the vessel. Fill the absorbing vessel with 35ml. of the zinc acetate solution. Connect each part of the apparatus as shown in Fig. 1., and pass carbon dioxide very rapidly for five minutes to expel the air in the reaction and the absorption vessel. The passage of the gas should be rapid enough to cause strong agitation of the surface of the liquid in the absorption vessel. The end of the gas delivery tube should reach to the bottom of the absorption vessel. At the end of five minutes, reduce the flow of the gas to a rate of one bubble per second. Heat the reaction vessel on the small electric heater (E), which is regulated by a variable transformer, till white fumes of phosphoric acid appear. Continue the heating for about fifteen minutes. It is unnecessary to keep the temperature strictly constant but it should be high enough to ensure that the content in the reaction vessel exhibits a white turbidity near the end of the fifteen minutes. Stop the heating and continue to pass carbon dioxide about five minutes.

Remove the absorption vessel and keep it in a thermostat for several minutes at 24°C. Add quickly 1.5 ml. of *p*-aminodimethylaniline solution using a rapid delivery pipet, stopper the vessel and shake it vigorously, and then quickly add 0.5 ml. of ferric chloride solution. Stopper and shake vigorously the vessel again. After keeping the vessel in the thermostat at 24°C. for fifteen minutes, remove the delivery tube from the solution, washing down the adhering solution into the vessel with distilled water. Add more distilled water till the liquid reaches the 50 ml. mark. Read the absorbancy of the solution in the colorimeter at 655 mμ within thirty minutes. According to the authors' experience, main sources of error in this method seem to be imperfect removal of oxygen from the carbon dioxide and careless delay in adding the colorization reagents viz., *p*-aminodimethylaniline and ferric chloride.

A standard calibrating curve, showing the relation between the amounts of sulfur taken and the absorbancies measured, should be prepared by carrying out the procedure with the standard sodium sulfate solution in the range 1 to 40 micrograms of sulfur. Estimate the amount of organic sulfur in the sample analyzed by comparing the absorbancy measured with this calibration curve. Use a mixture of the absorbing solution and the reagents of the definite amounts as reference for the photoelectric measurement.

Results and Discussion

Behavior of Chromium(VI)-Strong Phosphoric Acid.—This oxidizing agent is so powerful that all organic compounds, even coal, are completely oxidized at a temperatures below 200°C. Moreover, it has the advantageous property that all of the chromium(VI) remaining unchanged can be decomposed to chromium(III) easily

by further heating, so that no excess of chromium(VI) will remain and consume the tin(II)-strong phosphoric acid in the succeeding reduction process. This chemical property of chromium(VI)-strong phosphoric acid is very interesting and advantageous not only for this purpose but for many other oxidizing processes.

Results of Analysis.—Analyses of some known organic compounds containing sulfur were carried out by this method. Each sample was first dried in an Abderhalden's apparatus at a suitable temperature for the compound, and weighed accurately. The weighed sample was dissolved in a definite volume of water, in some cases with the aid of a small amount of hydrochloric acid. An aliquot from the solution was employed for the analysis. By the measurement of the absorbancy of the methylene blue color produced in each case, the amount of sulfur in the sample tested was calculated by means of the equation:

$$x=0.047+0.01478y$$

where x is the absorbancy measured and y is the amount of sulfur in micrograms. The equation was derived from many experimental data obtained by carrying out the procedure with sodium sulfate as the standard. The numerical values in the equation, as a matter of course, were calculated by the method of the least square from the experimental data. The constant, 0.047 represents the sulfur contained as an impurity in the reagents used, viz., potassium dichromate and the diluted tin(II)-strong phosphoric acid. The numerical values in the equation will depend on the sulfur contained in the reagents as well as on the spectral purity of the photoelectric colorimeter employed. The results obtained with some organic compounds are listed in Tables I to VI.

TABLE I

DETERMINATION OF SULFUR IN SULFUR GUANIDINE

Sample taken μg.	Sulfur contained μg.	Absorbancy measured	Sulfur found μg.	Recovery of sulfur %
0.	0.	0.047	0.	
13.4	2.	0.0762	1.98	99.0
40.1	6.	0.1355	5.99	99.8
66.8	10.	0.1948	10.00	100.0
100.2	15.	0.2688	15.01	100.1
133.6	20.	0.3469	20.02	100.1
167.0	25.	0.4160	24.97	99.9
200.6	30.	0.4896	29.95	99.8
233.9	35.	0.5630	34.91	99.7

TABLE II

DETERMINATION OF SULFUR IN METHYL ORANGE

Sample taken μg.	Sulfur contained μg.	Absorbancy measured	Sulfur found μg.	Recovery of sulfur %
0.	0.	0.047	0.	
20.4	2.	0.0760	1.96	98.0
61.3	6.	0.1353	5.97	99.5
102.1	10.	0.1946	9.97	99.7
153.1	15.	0.2686	14.99	99.9
204.2	20.	0.3545	19.99	99.9
255.2	25.	0.4276	24.94	99.8
306.3	30.	0.5010	29.91	99.7
357.3	35.	0.5745	34.88	99.7

TABLE III

DETERMINATION OF SULFUR IN *l*-CYSTINE

Sample taken μg.	Sulfur contained μg.	Absorbancy measured	Sulfur found μg.	Recovery of sulfur %
0.	0.	0.047	0.	
7.5	2.	0.0745	1.86	93.0
22.5	6.	0.1482	5.90	98.3
37.5	10.	0.2078	9.93	99.3
56.2	15.	0.2819	14.95	99.6
74.9	20.	0.3415	19.93	99.7
93.7	25.	0.4198	24.95	99.8
112.4	30.	0.5030	29.90	99.7
131.1	35.	0.5760	34.84	99.5

TABLE IV

DETERMINATION OF SULFUR IN *l*-METHIONINE

Sample taken μg.	Sulfur contained μg.	Absorbancy measured	Sulfur found μg.	Recovery of sulfur %
0.	0.	0.047	0.	
9.3	2.	0.0746	1.87	93.5
27.9	6.	0.1350	5.95	99.2
46.5	10.	0.1938	9.93	99.3
69.8	15.	0.2685	14.99	99.9
93.1	20.	0.3419	19.95	99.8
116.3	25.	0.4150	24.90	99.6
139.6	30.	0.4890	29.90	99.7
162.9	35.	0.5626	34.88	99.6

TABLE V

DETERMINATION OF SULFUR IN THIOUREA

Sample taken μg.	Sulfur contained μg.	Absorbancy measured	Sulfur found μg.	Recovery of sulfur %
0.	0.	0.047	0.	
4.7	2.	0.0748	1.88	94.0
14.2	6.	0.1340	5.89	98.2
23.7	10.	0.1930	9.88	98.8
35.6	15.	0.2670	14.88	99.2
47.5	20.	0.3410	19.21	95.6
59.4	25.	0.4050	24.22	96.9
71.2	30.	0.4884	29.86	99.5
83.1	35.	0.5284	34.80	99.4

TABLE VI
DETERMINATION OF SULFUR IN CRESOL RED

Sample taken γg.	Sulfur contained γg.	Absorbancy measured	Sulfur found γg.	Recovery of sulfur %
0.	0.	0.047	0.	
23.9	2.	0.0755	1.93	96.5
71.6	6.	0.1356	5.99	99.5
119.3	10.	0.1948	9.99	99.9
178.9	15.	0.2690	15.02	100.1
238.5	20.	0.3388	19.74	98.7
298.2	25.	0.4165	25.00	100.0
357.8	30.	0.4900	29.97	99.9
417.4	35.	0.5635	34.95	99.9

In the column under "Recovery of sulfur" is given the ratio in percentage of sulfur found to the amount taken in each case.

Preliminary Elimination of Sulfur from the Reagents.—As described in the above section, strong phosphoric acid, prepared from commercial orthophosphoric acid (D=1.7), always contains a minute amount of sulfur as impurity. In order to eliminate the sulfur the authors have prepared the diluted tin(II)-strong phosphoric acid as described above. The amounts of sulfur contained in the untreated strong phosphoric acid and in the diluted tin(II)-strong phosphoric acid were determined by carrying out the same reduction procedure. The results are shown in Table VII, which shows that the sulfur contained in the original strong phosphoric acid was expelled almost completely by treating with as little as 1 g. of tin(II) chloride dihydrate. The contents of sulfur in potassium dichromate reagent were estimated by the same procedure, and the results are tabulated all together in Table VII.

TABLE VII
SULFUR CONTENT IN THE REAGENTS AND ITS ELIMINATION

Reagent	Amount taken ml.	Absorbancy measured	Sulfur found in 1 ml. of the reagent γg.
Strong phosphoric acid	1	0.2229	15.1
	1	0.1852	12.5
Diluted tin(II)-strong phosphoric acid (A)	1	0.011	0.74
	1	0.013	0.87
Diluted tin(II)-strong phosphoric acid (B)	1	0.013	0.87
	1	0.013	0.87
Mixture of 100 g. of tin(II)-strong phosphoric acid (A) and 6 g. of $K_2Cr_2O_7$ (C)	1	0.027	1.82
	1	0.024	1.62
Mixture of 100 g. of tin(II)-strong phosphoric acid (B) and 12 g. of $K_2Cr_2O_7$ (C)	1	0.044	2.98
	1	0.050	3.38
Mixture of 100 g. of tin(II)-strong phosphoric acid (A) and 6 g. of $K_2Cr_2O_7$ (D)	1	0.062	4.19
	1	0.051	3.45

Note:

Diluted tin(II)-strong phosphoric acid (A) was prepared from 100 g. of strong phosphoric acid and 1 g. of tin(II)-chloride dihydrate; (B) from 100 g. of the acid and 5 g. of the salt.

$K_2Cr_2O_7$ (C) was a standard reagent supplied by Osaka Goverment Industrial Research Institute; (D) was a commercial reagent recrystallized in the laboratory.

Summary

A simple and rapid method for the determination of minute amounts of organic sulfur was established by using the oxidizing action of chromium(VI)-strong phosphoric acid and the reducing power of tin(II)-strong phosphoric acid. Organic sulfur was oxidized to sulfate by the former in a test-tube of fused silica and the sulfate was reduced to hydrogen sulfide by the latter in the same vessel. The hydrogen sulfide evolved was absorbed in zinc acetate solution and estimated colorimetrically by the ordinary methylene blue method. The absorbancy of the colored solution was measured at 655 mμ with a photoelectric colorimeter using 1-cm. cells. The sulfur content of the sample was estimated by comparing the absorbancy value with the standard curve prepared with sodium sulfate. Some organic compounds containing sulfur were analyzed by this method and satisfactory results were obtained. However, analysis of the miscellaneous organic substances such as biological specimens has not been undertaken and the problems for this purpose remain to be solved in future.

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Normal Vibrations of Tetramethylmethane and Tetramethylmethane-d_{12}

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The Wilson *FG* matrix method for the tetrahedral $M(XY_3)_4$ molecules has been used by Siebert[1] But no symmetry coordinates were given and a valence force field, including only one cross term of M–X and X–M–X internal coordinates, was used. The present investigation was undertaken in an attempt to carry out a normal coordinate treatment with a Urey-Bradley potential function and to assign observed frequencies for $C(CH_3)_4$ and $C(CD_3)_4$ to fundamental modes of vibration.

Normal Coordinate Treatment

A representation of the forty-five normal vibrational modes of the tetrahedral $M(XY_3)_4$ molecules is reduced to fourteen by $\Gamma=3a_1+4e+7f_2$. According to the well-known selection rules, all fundamentals are allowed in Raman spectrum, while only type f_2 fundamentals are allowed in the infrared. In the Raman spectrum, the a_1 vibrations correspond to polarized lines, the others to depolarized. It is possible to show that in both the a_1 and e species, $n^{(\Gamma)}=1$ for any sets of equivalent internal coordinates, while in the f_2 species, $n^{(\Gamma)}=2$ for the X–Y stretching and the Y–X–Y bending coordinates. For the latter case, it is neccesary to find K, which is a subgroup of G, and to construct the final symmetry coordinates from nondegenerate symmetry coordinates under K, as shown in the following manner:

$G(T_d)$	$K(C_{2v})$	Symmetry coordinates	
	a_1	R_9,	R_{11}
f_2	b_1	R_8,	R_{10}
	b_2	None	

From the internal coordinates (Fig. 1), the following orthonormal symmetry coordinates were formed:

for the a_1 vibrations,

$$R_1=\Delta(y_{11}+y_{12}+y_{13}+y_{21}+y_{22}+y_{23}+y_{31}+y_{32}+y_{33}+y_{41}+y_{42}+y_{43})/12^{1/2},$$

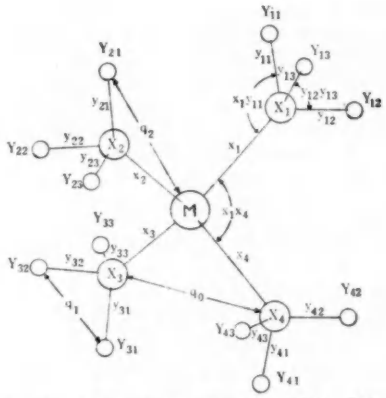

Fig. 1. Internal coordinates of $M(XY_3)_4$ molecule.

$$R_2=\Delta(y_{11}y_{12}+y_{11}y_{13}+y_{12}y_{13}+y_{21}y_{22}+y_{21}y_{23}+y_{22}y_{23}+y_{31}y_{32}+y_{31}y_{33}+y_{32}y_{33}+y_{41}y_{42}+y_{41}y_{43}+y_{42}y_{43}-x_1y_{11}-x_1y_{12}-x_1y_{13}-x_2y_{21}-x_2y_{22}-x_2y_{23}-x_3y_{31}-x_3y_{32}-x_3y_{33}-x_4y_{41}-x_4y_{42}-x_4y_{43})/24^{1/2},$$ and

$$R_3=\Delta(x_1+x_2+x_3+x_4)/2:$$

for the e vibrations,

$$R_{4a}=\Delta(2y_{11}-y_{12}-y_{13}+2y_{21}-y_{22}-y_{23}+2y_{31}-y_{32}-y_{33}+2y_{41}-y_{42}-y_{43})/24^{1/2},$$

$$R_{5a}=\Delta(2y_{12}y_{13}-y_{11}y_{12}-y_{11}y_{13}+2y_{22}y_{23}-y_{21}y_{22}-y_{21}y_{23}+2y_{32}y_{33}-y_{31}y_{32}-y_{31}y_{33}+2y_{42}y_{43}-y_{41}y_{42}-y_{41}y_{43})/24^{1/2},$$

$$R_{6a}=\Delta(2x_1y_{11}-x_1y_{12}-x_1y_{13}+2x_2y_{21}-x_2y_{22}-x_2y_{23}+2x_3y_{31}-x_3y_{32}-x_3y_{33}+2x_4y_{41}-x_4y_{42}-x_4y_{43})/24^{1/2},$$ and

$$R_{7a}=\Delta(2x_1x_2-x_1x_3-x_1x_4+2x_2x_3-x_2x_4-x_2x_4)/12^{1/2};$$

for the f_2 vibrations,

$$R_{8a}=\Delta(2y_{21}-y_{22}-y_{23}+2y_{31}-y_{32}+2y_{42}-y_{43}-y_{41})/18^{1/2},$$

$$R_{9a}=\Delta(3y_{11}+3y_{12}+3y_{13}-y_{21}-y_{22}-y_{23}-y_{31}-y_{32}-y_{33}-y_{41}-y_{42}-y_{43})/6,$$

$$R_{10a}=\Delta(2y_{22}y_{23}-y_{21}y_{22}-y_{21}y_{23}+2y_{31}y_{32}-y_{31}y_{33}-y_{32}y_{33}+2y_{41}y_{43}-y_{41}y_{42}-y_{42}y_{43})/18^{1/2},$$

$$R_{11a}=\Delta(3y_{11}y_{12}+3y_{11}y_{13}+3y_{12}y_{13}-y_{21}y_{22}-y_{21}y_{23}-y_{22}y_{23}-y_{31}y_{32}-y_{31}y_{33}-y_{32}y_{33}$$

1) H. Siebert, *Z. anorg. allgem. Chem.*, **268**, 177 (1952).

$$-y_{11}y_{12}-y_{11}y_{13}-y_{12}y_{13}-3x_1y_{11}-3x_1y_{12}$$
$$-3x_1y_{13}+x_2y_{21}+x_2y_{22}+x_2y_{23}+x_3y_{31}$$
$$+x_3y_{32}+x_3y_{33}+x_1y_{11}+x_1y_{12}$$
$$+x_1y_{13})/72^{1/2},$$

$$R_{12d}=\Delta(3x_1-x_2-x_3-x_1)/12^{1/2},$$

$$R_{13a}=\Delta(2x_2y_{21}-x_2y_{22}-x_2y_{23}+2x_3y_{33}-x_3y_{31}$$
$$-x_3y_{32}+2x_1y_{42}-x_1y_{11}-x_1y_{13})/18^{1/2}, \text{ and}$$

$$R_{14a}=\Delta(x_1x_2+x_1x_3+x_1x_4-x_2x_3-x_2x_4$$
$$-x_3x_4)/6^{1/2}.$$

The numbering of these coordinates corresponds to the numbering of the fundamentals in Table III.

From the potential constants of a Urey-Bradley force field[2] and the coefficients of the symmetry coordinates, one obtains the following F matrix elements:

for the a_1 vibrations,

$$F_{11}=K_1+4s_1^2F_1+t_2^2F_2'+s_2^2F_2,$$
$$F_{12}=2^{1/2}t_1s_1(F_1'+F_1)y-(t_2s_2F_2'$$
$$+t_3s_2F_2)x/2^{1/2},$$
$$F_{13}=3^{1/2}(-t_2t_3F_2'+s_2s_3F_2),$$
$$F_{22}=[(H_1-s_1^2F_1'+t_1^2F_1)y^2+(H_2-s_2s_3F_2'$$
$$+t_2t_3F_2)xy+3k_1/2^{1/2}]/2,$$
$$F_{23}=-3^{1/2}(t_3s_2F_2'+t_2s_3F_2)y/2^{1/2}, \quad \text{and}$$
$$F_{33}=K_0+6s_02F_0+3t_3^2F_2'+3s_3^2F_2;$$

for the e vibrations,

$$F_{11}=K_1+3t_1^2F_1'+s_1^2F_1+t_2^2F_2'+s_2^2F_2,$$
$$F_{12}=-t_1s_1(F_1'+F_1)y,$$
$$F_{13}=(t_2s_2F_2'+t_3s_2F_2)x,$$
$$F_{22}=(H_1-s_1^2F_1+t_1^2F_1)y^2+2^{1/2}k_1/4,$$
$$F_{23}=k_1/2^{1/2},$$
$$F_{33}=(H_2-s_2s_3F_2'+t_2t_3F_2)xy+2^{1/2}k_1/4,$$
$$F_{44}=(H_0-s_0^2F_0'+t_0^2F_0)x^2-2^{1/2}k_0/4, \text{ and}$$
$$F_{14}=F_{24}=F_{34}=0;$$

and for the f_2 vibrations,

$$F_{11}=K_1+3t_1^2F_1'+s_1^2F_1+t_2^2F_2'+s_2^2F_2,$$
$$F_{13}=-t_1s_1(F_1'+F_1)y,$$
$$F_{16}=(t_2s_3F_2'+t_3s_2F_2)x,$$
$$F_{22}=K_1+4s_1^2F_1+t_2^2F_2'+s_2^2F_2,$$
$$F_{24}=2^{1/2}t_1s_1(F_1'+F_1)y-(t_2s_3F_2'$$
$$+t_3s_2F_2)x/2^{1/2},$$
$$F_{25}=3^{1/2}(-t_2t_3F_2'+s_2s_3F_2),$$
$$F_{33}=(H_1-s_1^2F_1'+t_1^2F_1)y^2+2^{1/2}k_1/4,$$
$$F_{36}=-k_1/2^{1/2},$$
$$F_{44}=[(H_1-s_1^2F_1'+t_1^2F_1)y^2+(H_2-s_2s_3F_2'$$
$$+t_2t_3F_2)xy+3k_1/2^{1/2}]/2$$
$$F_{45}=-3^{1/2}(t_3s_2F_2'+t_2s_3F_2)y/2^{1/2},$$
$$F_{55}=K_0+4t_0^2F_0'+2s_0^2F_0+3t_3^2F_2'+3s_3^2F_2,$$
$$F_{57}=2^{1/2}t_0s_0(F_0'+F_0)x,$$
$$F_{66}=(H_2-s_2s_3F_2'+t_2t_3F_2)xy+2^{1/2}k_1/4,$$
$$F_{77}=(H_0-s_0^2F_0'+t_0^2F_0)x^2+3k_0/8^{1/2}, \text{ and}$$

$$F_{12}=F_{14}=F_{15}=F_{17}=F_{23}=F_{26}=F_{27}=F_{34}=F_{35}$$
$$=F_{37}=F_{46}=F_{47}=F_{56}=F_{67}=0,$$

where the following abbreviations are adopted:

$$t_0=8^{1/2}x/3q_0, \quad t_1=8^{1/2}y/3q_1, \quad t_2=8^{1/2}x/3q_2,$$
$$t_3=8^{1/2}y/3q_2, \quad s_0=4x/3q_0, \quad s_1=4y/3q_1,$$
$$s_2=(x+3y)/3q_2, \quad s_3=(3x+y)/3q_2,$$

and the symbols used for the equilibrium values of the interatomic distances are

$$x=M-X, \quad y=X-Y, \quad q_0=X\cdots\cdots X,$$
$$q_1=Y\cdots\cdots Y, \text{ and } q_2=M\cdots\cdots Y.$$

The G matrix elements, obtained by use of the table of Decius[3] and the method of Crawford[4], are as follows:

for the a_1 vibration,

$$G_{11}=\mu_X/3+\mu_Y,$$
$$G_{12}=-4\mu_X/3y,$$
$$G_{13}=-\mu_X/3^{1/2},$$
$$G_{22}=2(8\mu_X/3+\mu_Y)/y^2,$$
$$G_{23}=4\mu_X/3^{1/2}y, \text{ and}$$
$$G_{33}=\mu_X;$$

for the e vibrations,

$$G_{11}=4\mu_X/3+\mu_Y,$$
$$G_{12}=32^{1/2}\mu_X/3y,$$
$$G_{13}=-2^{1/2}\mu_X(3/x+1/y)/3,$$
$$G_{14}=2\mu_X/x,$$
$$G_{22}=(8\mu_X/3+5\mu_Y/2)/y^2,$$
$$G_{23}=-2\mu_X(1/3y^2+1/xy)+\mu_Y/2y^2,$$
$$G_{24}=8^{1/2}\mu_X/xy,$$
$$G_{33}=\mu_X(3/2x^2+1/xy+1/6y^2)+\mu_Y/y^2.$$
$$G_{34}=-\mu_X(3/x^2+1/xy)/2^{1/2}, \text{ and}$$
$$G_{44}=3\mu_X/x^2;$$

and for the f_2 vibrations.

$$G_{11}=4\mu_X/3+\mu y,$$
$$G_{13}=32^{1/2}\mu_X/3y,$$
$$G_{16}=-2^{1/2}\mu_X(1/x+1/3y),$$
$$G_{17}=8^{1/2}\mu_X/3^{1/2}x,$$
$$G_{22}=\mu_X/3+\mu_Y,$$
$$G_{24}=-4\mu_X/3y,$$
$$G_{25}=-\mu_X/3^{1/2},$$
$$G_{33}=8\mu_X/3y^2+5\mu_Y/2y^2),$$
$$G_{36}=-2\mu_X(1/xy+1/3y^2)+\mu_Y/2y^2,$$
$$G_{37}=4\mu_X/3^{1/2}xy,$$
$$G_{44}=16\mu_X/3y^2+2\mu_Y/y^2,$$
$$G_{15}=4\mu_X/3^{1/2}y,$$
$$G_{55}=4\mu_M/3+\mu_X,$$
$$G_{59}=4\mu_M/3^{1/2}x,$$
$$G_{57}=-8\mu_M/3x,$$
$$G_{66}=4\mu_M/x^2+\mu_X(3/2x^2+1/xy+1/6y^2)$$
$$+\mu_Y/y^2,$$

2) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

3) J. C. Decius, *J. Chem. Phys.*, **16**, 1025 (1948).

4) B. Crawford, Jr., *J. Chem. Phys.*, **21**, 1108 (1953).

TABLE I

RAMAN AND INFRARED SPECTRAL DATA FOR TETRAMETHYLMETHANE

Type	Silver[a] (Raman)	YKM[b] (Infrared)	Sheppard[c] (Raman)	Siebert[d] (Raman)	SOR (Raman)	SOR (Infrared)
a_1	2913	2911	—	2911	2909	—
	1455	1252	—	—	—	—
	—	733	733	733	733	—
e	2957	2955	—	2955	—	—
	1455	1455	—	1455	1451	—
	925	925	925	—	—	—
	—	335	335	335	335	—
f_2	—	2962	—	2962	2955	2959
	—	2876	—	2876	—	2876
	—	1455	—	1455	—	1475
	—	1370	—	1370	—	1372
	—	1280	1252	1257	1249	1256
	—	925	925	925	921	925
	—	414	414	414	415	418

a See reference 5; b YKM=Young, Koehler and Mckinney, reference 6; c See reference 7; d See reference 1; e SOR=Shull, Oakwood and Rank, reference 9.

$G_{57}=-8\mu_M/3^{1/2}x^2-\mu_X(3^{1/2}/x^2+1/3^{1/2}xy)$,
$G_{77}=16\mu_M/3x^2+2\mu_X/x^2$, and
$G_{12}=G_{14}=G_{15}=G_{23}=G_{26}=G_{27}=G_{34}=G_{35}=G_{46}=G_{47}=0$.

Here μ_M, μ_X and μ_Y are, respectively, the reciprocals of the masses of the M, X and Y atoms.

Normal Frequencies of Tetramethylmethane

The Raman or the infrared spectral data and the assignments of the observed frequencies for tetramethylmethane have been obtained in previous investigations[1,5-9]. A summary of the fundamentals is given in Table I. A partial normal coordinate treatment was carried out by Silver[5] and by Sheline et al.[8] for the a_1 and e vibrations. Recently, Siebert[1] published the normal coordinate treatment of all vibrations. The disagreement between the results of the different investigations lies in the assignment of two of type f_2 vibrations, i.e. C—C stretching and CH_3 rocking vibration. In this paper, the nature of these vibrations will be clarified. Using the F and G matrix elements given above, the fundamental frequencies were calculated and shown in Table III. Probable values of the observed frequencies and assignment of the Raman and the infrared bands are included in the table. The molecular and potential constants used are listed in Table II. The C—H stretching vibrations were split off by the method of Wilson. The agreement between the calculated and observed fundamentals was almost completely satisfactory. The L

TABLE II

MOLECULAR AND POTENTIAL CONSTANTS OF $C(CH_3)_4$ AND $C(CD_3)_4$

Bond distance	Type	Potential constant (md/A) Set I	Set II
x=C—C	K_0(C—C)	3.440	2.474
=1.55A	H_0(C—C—C)	0.206	0.105
y=C—H	F_0(C·····C)	0.333	0.571
=C—D	k_0(CC_4)	0.040A^2	0.015A^2
=1.09A	K_1(C—H)	4.50	4.50
	H_1(H—C—H)	0.40	0.40
	H_2(C—C—H)	0.15	0.15
	F_1(H·····H)	0.10	0.10
	F_2(C·····H)	0.40	0.40
	k_1(CCH_3)	0.05A^2	0.05A^2
	F'	$-F/10$	$-F/10$

The potential constants for the skeletal vibrations were obtained from the observed frequencies of $C(CH_3)_4$:

The values of set I correspond to $\nu_1=733$, $\nu_2=335$, $\nu_3=1089$, and $\nu_4=414\,cm^{-1}$ and those of set II, to $\nu_1=733$, $\nu_2=335$, $\nu_3=925$, and $\nu_4=414\,cm^{-1}$ respectively.

The potential constants for the inner vibrations were obtained directly from the normal frequencies of $H_3C—CH_3$.

5) S. Silver, *J. Chem. Phys.*, **8**, 919 (1940).
6) C. W. Young, J. S. Koehler and D. S. Mckinney, *J. Am. Chem. Soc.*, **69**, 1410 (1947).
7) N. Sheppard, *J. Chem. Phys.*, **16**, 690 (1948).
8) R. K. Sheline and K. S. Pitzer, *J. Chem. Phys.*, **18**, 595 (1950).
9) E. R. Shull, T. S. Oakwood and D. H. Rank, *J. Chem. Phys.*, **21**, 2024 (1953).

TABLE III

PROBABLE VALUES OF THE OBSERVED FUNDAMENTALS, CALCULATED WAVE NUMBERS, AND ASSIGNMENTS FOR $C(CH_3)_4$.

Type	Assignment: Frequency	Mode of vibration	ν calc. Set I	ν calc. Set II	ν obs.
a_1	ν_1	CH_3 sym. str.	2932	2932	2909
	ν_2	CH_3 sym. def.	1395	1395	—
	ν_3	C—C skel. str.	791	790	733
e	ν_4	CH_3 nonsym. str.	2984	2984	2955
	ν_5	CH_3 nonsym. def.	1443	1442	1451
	ν_6	CH_3 rocking	905	905	925
	ν_7	C—C—C skel. def.	308	307	335
f_2	ν_8	CH_3 nonsym. str.	2984	2984	2959
	ν_9	CH_3 sym. str.	2932	2932	2876
	ν_{10}	CH_3 nonsym. def.	1442	1442	1475
	ν_{11}	CH_3 sym. def.	1390	1377	1372
	ν_{12}	CH_3 skel. str.	1272	1160	1256
	ν_{13}	CH_3 rocking	873	852	925
	ν_{14}	C—C—C skel. def.	372	367	418

matrices, whose components give the modes of vibrations, and the potential energy distributions for the questionable two triply degenerate vibrations were calculated and shown in Tables IV and V. Judging from the values of the contribution of each sym-

TABLE IV

L-MATRICES OF TWO TYPE f_2 VIBRATIONS OF C $(CH_3)_4$.

f_2	Q_{12} Set I	Q_{12} Set II	Q_{13} Set I	Q_{13} Set II
R_{10}	−0.09	−0.09	−0.07	−0.05
R_{11}	−0.36	−0.00	0.06	0.03
R_{12}	0.36	0.34	−0.16	−0.22
R_{13}	0.64	0.67	0.83	0.72
R_{14}	−0.41	0.36	−0.04	0.01

TABLE V

POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR ν_{12} AND ν_{13} VIBRATIONS

f_2	ν_{12} Set I	ν_{12} Set II	ν_{13} Set I	ν_{13} Set II
R_{10}	0.00	0.01	0.00	0.00
R_{11}	0.13	0.00	0.01	0.00
R_{12}	0.65	0.57	0.28	0.45
R_{13}	0.19	0.25	0.68	0.53
R_{14}	0.06	0.06	0.00	0.00

metry coordinate to the normal coordinate Q_{12} in Table IV, it is no longer accurate to designate the frequency ν_{12} as only one mode of vibration, i.e., "C—C stretching". However, it can be seen that, by taking into consideration the distribution of energy in the symmetry coordinates in Table V, the classification given in Table III is reasonable. On the contrary, it is undubitable that the frequency ν_{13}, which is relatively pure, can be assigned to "CH_3 rocking".

Normal Frequencies of Tetramethylmethane-d_{12}

The Raman and the infrared spectral data and the assignments of the observed frequencies for tetramethylmethane-d_{12} have been reported by Shull et al.[9], but a normal coordinate treatment has not been carried out in the literature. According to them, since the observed frequency 765 cm^{-1} is analogous to the band at 921 cm^{-1} in tetramethylmethane, it should be assigned to "C—C stretching" and the observed frequency 1218 cm^{-1} can be assigned to "CD_3 rocking". In general, a normal mode of vibration in which the hydrogen atom in question oscillates with a relatively large amplitude will suffer a greater isotopic change in frequency than that of a normal mode in which this hydrogen moves with a relatively small amplitude. Since the ratio 765/921 is nearly equal to a theoretically expected value $1/2^{1/2}$, it is probably rigorous to designate the frequency observed at 765 cm^{-1} as "CD_3 rocking". Since the frequencies observed at about 1200 cm^{-1} maintain a constant value in both the ordinary and deuterated compounds, it is reasonable to assign these frequencies to "C—C stretching". Using the F and G matrix elements given above, the fundamental frequencies were calculated and shown in Table VI with

TABLE VI

OBSERVED AND CALCULATED FONDAMENTAL FREQUENCIES AND ASSIGNMENTS FOR $C(CD_3)_4$

Type	Assignment: Frequency	Mode of vibration	ν calc. Set I	ν calc. Set II	ν obs.
a_1	ν_1	CD_3 sym. str.	2110	2110	2128
	ν_2	CD_3 sym. def.	1130	1130	1104
	ν_3	C—C skel. str.	684	684	648
e	ν_4	CD_3 nonsym. str.	2221	2221	—
	ν_5	CD_3 nonsym. def.	1055	1055	1048
	ν_6	CD_3 rocking	695	694	—
	ν_7	C—C—C skel. def.	264	263	276
f_2	ν_8	CD_3 nonsym. str.	2221	2221	2218
	ν_9	CD_3 sym. str.	2110	2110	2058
	ν_{10}	C—C skel. str.	1279	1150	1218
	ν_{11}	CD_3 nonsym. def.	1058	1057	1066
	ν_{12}	CD_3 sym. def.	1029	1020	1037
	ν_{13}	CD_3 rocking	684	679	765
	ν_{14}	C—C—C skel. def.	316	311	342

those observed by Shull et al. The calculation of the L matrix elements (Table VII) and of the potential energy distributions (Table VIII) shows that the assignments given in Table VI are more reasonable.

TABLE VII
L-MATRICES OF TWO TYPE f_2 VIBRATIONS OF $C(CD_3)_4$

f_2	Q_{10} Set I	Q_{13} Set I
R_{10}	−0.04	0.02
R_{11}	0.51	0.13
R_{12}	0.42	−0.10
R_{13}	0.41	0.62
R_{14}	−0.36	−0.10

TABLE VIII
POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR ν_{10} AND ν_{13} VIBRATIONS

f_2	ν_{10} Set I	ν_{13} Set I
R_{10}	0.00	0.00
R_{11}	0.15	0.04
R_{12}	0.87	0.17
R_{13}	0.09	0.72
R_{14}	0.11	0.03

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The Exhaustive Methylation of cis- and trans-Hexahydrocarbazoles[1]

By Tadashi MASAMUNE

(Received January 14, 1957)

It has been established by King, Baltrop and Walley[2] that in the exhaustive methylation, *cis*-octahydroindole undergoes a fission of the N-C_8 bond to yield 1-(2-dimethylaminoethyl)-cyclohexene, while the corresponding *trans*-base produces no compound expected from the normal opening of the pyrrolidine ring. The methine $C_{10}H_{19}N$ (I) resulting from the *trans*-base was suggested to be II[3] and to be produced by a Wagner-Meerwein type rearrangement (a) of the carbonium ion (III) formed by ring-scission at C_8 (Fig. 1). However, the structure (II) was not verified experimentally. As it is desirable to investigate the behavior of similar compounds, the present author subjected *cis*- and *trans*-hexahydrocarbazoles to the exhaustive methylation. These bases may be regarded as analogs of octahydroindoles and are much more easily obtainable than *trans*-octahydroindole.

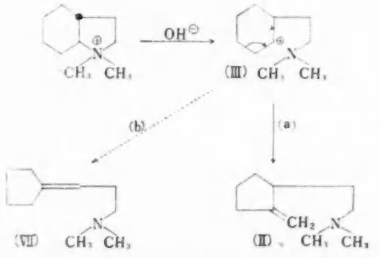
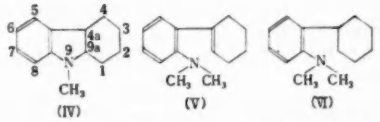


Fig. 1. The exhaustive methylation of *trans*-octahydro-N-methylindole methiodide.

Treatment of *cis*-hexahydrocarbazole and of its N-methyl-derivative (IV) with methyl iodide easily yielded the methiodide. Distillation of the compound obtained by treating an aqueous solution of the methiodide with silver oxide yielded an oily base, from which an unsaturated base $C_{11}H_{19}N$ (V) was isolated in a yield of 70%.



In order to determine its constitution the methine base (V) was subjected to

1) Part IX of "The Condensed Polynuclear Perhydro-Compounds Containing Nitrogen"; Part VIII, T. Masamune and M. Koshi, This Bulletin, **30**, 307 (1957).
2) F. E. King, J. A. Baltrop and R. J. Walley, *J. Chem. Soc.*, **1945**, 277; B. Bailey, R. D. Haworth and J. McKenna, ibid., **1954**, 967.
3) F. E. King and H. Booth, ibid., **1954**, 3798.

Emde reduction. The resulting hydrocarbon gave δ-benzoylvaleric acid on oxidation and thus was found to be 1-phenylcyclohexene. Then, it follows that the product from the exhaustive methylation is 1-(*o*-dimethylaminophenyl)-cyclohexene (V). That the double bond in the cyclohexene ring is conjugated with the phenyl ring is concluded from the following fact. Comparison of the ultraviolet spectra of the methine base (V) and its dihydro-derivative (VI) with that of N-dimethyl-*o*-toluidine indicated that

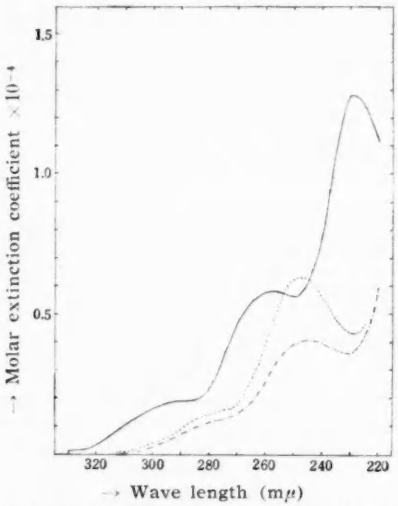


Fig. 2. Ultraviolet absorption spectra of *o*-toluidine derivatives.
Solvent: ethanol; conc. M×10⁻⁴
—— 1-(*o*-Dimethylaminophenyl)-cyclohexene (V)
- - - - *o*-Dimethylaminophenylcyclohexane (VI)
-·-·- N-dimethylamino-*o*-toluidine

there was no maximum in either of Doub's "secondary" bands[4] (Fig. 2). This may suggest that the bases are *o*-substituted N-dimethylanilines[5]. The absorption curves of base VI and N-dimethyl-*o*-toluidine had maxima at the almost identical wave length (247 mμ) of each "primary" band, whereas that of base V had a maximum at 259 mμ showing the existence of a double bond conjugated with the phenyl ring.

The formation of 1-(*o*-dimethylaminophenyl)-cyclohexene involves both fission of the N-C_{9a} bond and attack of the hydroxide ion on the most acidic β-hydrogen atom in a *trans*-position to the bond, and may be reasonable in the light of stereochemistry[6] and of Hofmann's rule[7].

Formation and decomposition of *trans*-hexahydro-N-methyl-carbazole methohydroxide were investigated analogously to the case of the *cis*-base. Then a mixture of two bases was produced, one being 1-(*o*-dimethylaminophenyl)-cyclohexene identical with the base resulting from the exhaustive methylation of the *cis*-base, and the other *cis*-hexahydro-N-methylcarbazole (IV). This result was borne out by the mixed melting point determination of their picrates with authentic specimens, by comparison of the ultraviolet spectra, and by dehydrogenation experiment. The yield of the former was 50% of the theoretical and that of the latter 25%.

With *trans*-hexahydro-N-methylcarbazole methohydroxide, the stereochemical effect required for the usual Hofmann degradation is not satisfied. Therefore, a rearranged base was expected to appear considering the behavior of *trans*-octahydro-N-methylindole in the exhaustive methylation. But no such base could be isolated and base V was obtained instead. This is probably attributable to the ease in the elimination of the acidic β-hydrogen at C_{4a} caused by the anilinium ion. Several examples of this type of elimination have already been reported[8]. On the other hand, the formation of base IV probably involves an elimination of methanol and a subsequent stereochemical rearrangement. Elimination of methanol is encountered in the exhaustive methylation of several alkaloids[9]. But no example is so far known of this type of elimination accompanied by a stereochemical rearrangment.

In the next place, the preparation of

4) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).
5) H. B. Klevens and J. R. Platt, ibid., **71**, 1714 (1949); W. R. Remington, ibid., **67**, 1838 (1945); H. E. Ungnade, ibid., **76**, 5133 (1954).
6) For reviews see W. Klyne in "Progress in Stereochemistry" ed. W. Klyne, Vol. 1. Butterworth's Scientific Publications, London (1954), p. 64.
7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University press, Ithaca, N. Y., (1953), p. 427.
8) J. Weinstock, R. G. Pearson and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 3473 (1956); E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, **1953**, 3832; S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2913 (1952); S. I. Miller and R. M. Noyes,ibid., **74**, 629 (1952).
9) Cuscohygrine, lupanine, matrine, etc., do not undergo a ring fission in the exhaustive methylation, methanol being eliminated. See, for example, T. A. Henry, "The Plant Alkaloids", 4th Ed., Churchill Ltd., London (1949), p. 103, 129 and 147; J. Read and J. Walker., *J. Chem. Soc.*, **1934**, 308; N. L. McNiven and J. Read, ibid., **1952**, 153, 159.

γ-dimethylaminopropylcyclopentane was undertaken, because this compound may be produced by the Hofmann degradation of *trans*-octahydroindole, if the Wagner-Meerwein type rearrangement of III proceeds through another possible course as indicated in Fig. 1 (b), and if the methine base (VII) thus formed is hydrogenated.

A Grignard reagent from cyclopentylmethyl bromide was treated with β-chloroethyl-*p*-toluenesulfonate to yield γ-cyclopentylpropyl chloride. The latter in ethanol was heated with dimethylamine in a closed vessel. γ-Dimethylaminopropylcyclopentane thus obtained was converted into the picrate, m.p. 108–110°, and into the picrolonate, m.p. 156–158°.

King et al.[9] reported that a hydrogenation product $C_{10}H_{21}N$ from I gave a picrate of m.p. 106° and a picrolonate of m.p. 160°. The present author's substances may be identical with theirs, but a direct comparison has not yet been possible because *trans*-octahydroindole is not easily available.

Experimental

***cis*-Hexahydro-N-methylcarbazole Methiodide.**—(a) Ten grams of *cis*-hexahydrocarbazole[10] was heated with 8.5 g. of methyl iodide in 40 cc. of ethanol for 6 hours on a water-bath. After removal of ethanol and methyl iodide under a reduced pressure, the residual oil was shaken for half an hour with 100 cc. of ether, 50 cc. of water, and 20 cc. of 6 N potassium hydroxide solution, when crystals insoluble in both layers precipitated. After separation of the ethereal solution by decantation, the precipitate was isolated from the alkaline solution by filtration. Treatment with hot acetone for half an hour on a water-bath and subsequent filtration gave the methiodide, m.p. 196–198°. Yield 3.3 g.

Anal. Found: C, 51.01; H, 5.95. Calcd. for $C_{14}H_{20}NI$: C, 51.07; H, 6.16%.

The ethereal solution was shaken with 3.5 g. of benzoyl chloride and N sodium hydroxide solution for 5 hours, separated from the alkali solution, treated with N hydrochloric acid, and evaporated to yield 4.2 g. of crude *cis*-hexahydro-N-benzoylcarbazole. Recrystallized from ethanol, the substance showed m. p. 103–105°.

The hydrochloric acid solution was made alkaline and the basic oil was collected with ether. On evaporation, the ethereal solution yielded 3 g. of *cis*-hexahydro-N-methylcarbazole[11], which gave a picrate melting at 144–145°.

Anal. Found: C, 54.99; H, 4.71. Calcd. for $C_{19}H_{20}N_4O_7$: C, 54.80; H, 4.84.%.

(b) A mixture of 3 g. of *cis*-hexahydro-N-methylcarbazole and 3 g. of methyl iodide was allowed to stand over night at the room temperature in a closed vessel. A crystalline substance thus obtained was collected by filtration. Recrystallization from acetone gave the methiodide, m.p. 196–197°. Further quantity of the methiodide, m.p. 193–195°, was obtained on concentration of the mother liquor and addition of ether. The total yield was 3.3 g.

***trans*-Hexahydro-N-methylcarbazole Methiodide.**—(a) A mixture of 2.3 g. of *trans*-hexahydrocarbazole[10] and 4.4 g. of methyl iodide in 15 cc. of ethanol was refluxed for 8 hours on a water-bath. After removal of ethanol and methyl iodide under a diminished pressure, the product was treated with 50 cc. of ether, 40 cc. of water, and 10 cc. of 6 N potassium hydroxide solution. The precipitate and the ethereal solution were separated similarly as from the *cis*-base. Treatment of the precipitate with 20 cc. of hot acetone gave 1.8 g, of *trans*-hexahydro-N-methylcarbazole methiodide, m.p. 233–234°.

Anal. Found: C, 51.46; H, 6.20. Calcd. for $C_{14}H_{20}NI$: C, 51.07; H, 6.16%.

The ethereal solution was shaken with benzoyl chloride and aqueous alkali and, after 4 hours, treated with N hydrochloric acid. Crude *trans*-hexahydro-N-benzoyl-carbazole (0.8 g.) from the ethereal solution was recrystallized from ethanol and showed m.p. 130–132°. The hydrochloric acid solution gave a solid base on alkalification. Recrystallization of the base from ethanol gave 0.4 g. of *trans*-hexahydro-N-methylcabazole, m.p. 59–61°.

Anal. Found: C, 83.57; H, 9.08. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15%.

Treatment of the base with picric acid in ethanol and recrystallization of the product from the same solvent yielded a pure picrate, m.p. 122–124°.

Anal. Found: C, 55.13; H, 4.66. Calcd. for $C_{19}H_{20}N_4O_7$: C, 54.80; H, 4.84%.

(b) A mixture of 1 g. of *trans*-hexahydro-N-methylcarbazole and 1 g. of methyl iodide was heated on a water-bath for one hour and the methiodide, m.p. 231–233°, was obtained substantially in a quantitative yield by a method similar to that used in the case of the *cis*-base.

Exhaustive Methylation of *cis*-Hexahydro-N-methylcarbazole Methiodide.—A solution of 3.5 g. of *cis*-hexahydro-N-methylcarbazole methiodide in a warm mixture of 30 cc. of water and 5 cc. of ethanol was shaken for 5 hours in the dark with silver oxide, freshly prepared from 2 g. of silver nitrate. The mixture was filtered and the filtrate was evaporated under a reduced pressure at about 60°. After most of the water was removed, the temperature was gradually raised. The syrupy quaternary hydroxide decomposed violently at 140–150°. The distillate was taken with ether and subjected to redistillation, yielding 1.4 g. (70%) of 1-(*o*-dimethylaminophenyl)-cyclohexene, b.p. 144–145° (12 mm.). Its

10) J. Gurney, W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, **1927**, 2676.

11) W. H. Perkin and S. G. P. Plant, ibid., **1924**, 1503.

12) K. V. Auwers and W. Treppmann, *Ber.*, **48**, 1207 (1915); L. F. Fieser and J. Szmuszkvicz, *J. Am. Chem. Soc.*, **70**, 3352 (1948).

picrate showed m.p. 165–167° on recrystallization from ethanol.

Anal. Found: C, 55.87; H, 4.98. Calcd. for $C_{20}H_{22}N_4O_7$: C, 55.81; H, 5.15%.

The methiodide of 1-(*o*-dimethylaminophenyl)-cyclohexene was prepared in the following manner. The base (5.5 g.) was refluxed with 17 g. of methyl iodide. In half an hour, a small amount (0.3 g.) of a crystalline substance was formed and collected by filtration. This salt had a formula $C_{14}H_{20}NI$, corresponding to a simple addition of methyl iodide to 1-(*o*-monomethylaminophenyl)-cyclohexene.

Anal. Found: C, 51.42, 51.00, 51.41; H, 5.88, 6.11, 6.14. Calcd. for $C_{14}H_{20}NI$: C, 51.07; H, 6.14%.

The solution separated from the salt was continuously refluxed for 60 hours, the precipitates thus formed being removed by filtration every 6 hours. The precipitates were combined and recrystallized from acetone. The purified methiodide decomposed at 195–196° (at 190–192° on slow heating), and amounted to 2.3 g.

Anal. Found: C, 52.45, 52.94: H, 6.24, 6.58. Calcd. for $C_{13}H_{22}NI$; C, 52.48; H, 6.47%.

The filtered solution gave 2 g. of unchanged 1-(*o*-dimethylaminophenyl)-cyclohexene on complete removal of methyl iodide.

1-(*o*-Dimethylaminophenyl)-cyclohexene (0.45g.) in 20 cc. of methanol was hydrogenated in the presence of 0.5g. of 10% palladium-charcoal at the room temperature under the atmospheric pressure for half an hour. After filtration, the solution was made slightly acidic with dil. hydrochloric acid and evaporated. The residue was treated with aqueous alkali and ether, and the ethereal solution gave 0.35 g. of oily dihydro-derivative. Its picrate showed m.p. 185–187° on recrystallization from ethanol.

Anal. Found: C, 55.20; H, 5.34. Calcd. for $C_{20}H_{24}O_4N_7$: C, 55.55; H, 5.59%.

Emde Reduction of 1-(*o*-Dimethylaminophenyl)-cyclohexene Methochloride. — 1-(*o*-Dimethylaminophenyl)-cyclohexene methiodide (2 g.) in 30 cc. of warm water was shaken for 45 minutes with silver chloride, freshly prepared from 10 g. of silver nitrate. The methochloride solution was filtered and heated on a water-bath with stirring, while 200 g. of sodium amalgam (5%) was added in portions during 6 hours. The resulting hydrocarbon was extracted with ether. From the ethereal solution 0.55 g. of the hydrocarbon[12], b.p. 134–136° (22mm.), was obtained.

Anal. Found: C, 91.04; H, 9.60. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92%. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06%.

The hydrocarbon (0.50 g.) was dissolved in a mixture of 35 cc. of acetone and 5 cc. of water, and 1 g. of potassium permanganate was added in portions at 40–50° during 2 hours. After addition of 10 cc. of water, the solution was filtered from manganese dioxide and concentrated on a water-bath. The residue was treated with ether to remove unchanged hydrocarbon and then acidified with conc. hydrochloric acid. The oil thus separated was collected with ether and solidified after removal of ether. Upon recrystallization from benzine, δ-benzoylvaleric acid, m.p. 72–74°, was obtained in a yield of 0.18 g. An authentic specimen[12] had m.p. 75–76°, and the mixed melting point was 73–75°.

Anal. Found: C, 69.50; H, 6.59. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

Treatment of this acid with semicarbazide hydrochloride and sodium acetate in aqueous ethanol and subsequent recrystallization from methanol gave its semicarbazone, m.p. 184–186°, the melting point being undepressed on admixture with an authentic specimen, m.p. 185–186°.

Anal. Found: C, 59.46; H, 6.43. Calcd. for $C_{13}H_{17}N_3O_3$: C, 59.30; H, 6.51%.

Exhaustive Methylation of *trans*-Hexahydro-N-methylcarbazole Methiodide. The reaction was carried out as already described for the *cis*-isomer. The quaternary hydroxide which was obtained by treatment of 2.8 g. of *trans*-hexahydro-N-methylcarbazole methiodide with silver oxide, prepared from 1.8 g. of silver nitrate, decomposed vigorously at 160–170°, a slightly higher temperature than in the case of the *cis*-isomer, and yielded 1.25 g. of an oil, b.p. 145–149° (13 mm.). Treatment of 0.5 g. of the base with 0.6 g. of picric acid in ethanol and two recrystallizations from the same solvent yielded 0.5 g. of the pure picrate, m.p. 168–170°, of 1-(*o*-dimethylaminophenyl)-cyclohexene, the melting point being undepressed in admixture with the picrate of the base obtained by the Hofmann degradation of the *cis*-base. The base (0.1 g.), regenerated from the picrate, was dehydrogenated with 0.4 g. of palladium charcoal (10%) at 280–300° for 30 minutes. An oil isolated by ether-extration of the reaction product was separated into a neutral and a basic fraction with 2N hydrochloric acid, the former (0.03 g.), m.p. 68–70°, being identified as biphenyl by the mixed melting point with an authentic specimen.

The ethanolic mother liquors of the picrate were combined and evaporated. The substance, obtained when the residue was refluxed with a small amount of acetone and the mixture was cooled, was again recrystallized from ethanol containing a small amount of acetone, yielding 0.25 g. of the picrate, m.p. 141–143°, of *cis*-hexahydro-N-methylcarbazole. The melting point was undepressed in admixture with an authentic specimen. An oily base (0.01 g.), obtained by decomposition of the picrate, was dehydrogenated with 0.03 g. of 10% palladium-charcoal at 220° for one hour to give 0.005g. of N-methylcarbazole, m.p. 84–86°, which was identified by the mixed melting point and by comparizon of ultraviolet spectra.

δ-Dimethylaminopropylcyclopentane. — A Grignard reagent was prepared from 10 g. of cyclopentylmethyl bromide[13], 1.5g. of magnesium, and a small amount of iodine in 15 cc. of ether, in a three-necked flask fitted with a separating funnel, a mechanical stirrer, and a reflux condenser. After addition of 5 cc. of ether, 24 g. of β-chloroethyl-*p*-toluenesulfonate[14] in 25 cc. of

13) C. R. Noller and R. Adams, ibid., **48**, 1080 (1926).
14) S. S. Rossander and C. S. Marvel, ibid., **50**, 1491 (1928).

ether was added with stirring during one hour at such a rate that the ether refluxed gently. The reaction mixture was then refluxed gently for 8 hours to give a large amount of a white precipitate. Additional ether was added from time to time in order to keep the mixture fluid enough for efficient stirring. The reaction mixture was then decomposed with cracked ice and treated with ether and enough dil. hydrochloric acid to dissolve the basic magnesium salts. The ethereal solution was subjected to distillation and a fraction, b.p. 68–80° (20 mm.), was collected, consisting mainly of γ-chloropropylcyclopentane.

Two grams of this fraction and 15 cc. of 15% ethanolic dimethylamine were heated in a sealed tube at 160–180° for 8 hours. The reaction mixture was made acidic with dil. hydrochloric acid and then ethanol was removed by evaporation. The residue was treated with ether and water. After separation of the ethereal solution, the aqueous solution was made alkaline and the oil thus formed was removed to ether. The ethereal solution gave 0.6 g. of an oil, b.p. 80–84° (20 mm.), on fractional distillation. This oil gave the picrate, m.p. 108–110°, of γ-dimethylaminopropylcyclopentane on treatment with picric acid and recrystallization from ethanol.

Anal. Found: C, 49.85; H, 6.00. Calcd. for $C_{16}H_{24}N_4O_7$: C, 49.99; H, 6.29%.

The picrolonate was prepared by dissolving the oil in an ethanolic solution of picrolonic acid. It showed m.p. 156–158° on recrystallization from ethanol.

Anal. Found: C, 57.16; H, 6.70. Calcd. for $C_{20}H_{29}N_5O_5$: C, 57.26; H, 6.97%.

The author acknowledges gratefully the supervision by Professor Harusada Suginome, President of Hokkaido University, under which the present research was carried out. Thanks are due to Mr. Minoru Inaba for his help in some of the preparations.

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Sedimentation of Spheres in a Suspension of Finite Concentration

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The sedimentation velocity in a centrifugal field supplies valuable information for the size and shape determination of colloidal particles and large molecules. Sedimentation velocity, however, is dependent on the concentration of particles in the suspension. Therefore, experimental values obtained by measurements performed on solutions or suspensions of finite concentration should be extrapolated to a value for infinite dilution in order to obtain information concerning the particle size and shape using the Stokes' law.

Stokes' law was calculated by using a model in which a sphere moved through a viscous fluid medium which extended infinitely in all directions, and the Reynolds' number was assumed to be very small. In cases of sedimentation experiments on molecular or colloidal suspensions the Reynolds' number is usually very small, and the latter condition is always satisfied. However, the cells used in sedimentation experiments are not infinite in size. Since the size of particles we are concerned with is so small, the volume of the sedimentation cell can be regarded as infinite when the concentration is very low. When the concentration is high, however, the distance between particles is comparable to the size of the particles, and the condition of flow around each particle is different from that in a case in which a particle is moving through an infinite medium.

When sedimentation coefficients vs. concentration curves for various substances are examined, they seem to coincide if the concentration axis is multiplied by a suitable factor. Thus if we exactly know the situation of sedimenting spheres, we can imagine a similar situation for sedimenting molecules and colloidal particles.

A number of studies on the concentration dependene of sedimentation coefficients[1-5] have appeared in the past and

1) R. E. Powell and H. Eyring, *Advances in Colloid Science*, **1**, 183 (1942).
2) J. M. Burgers, *Proc. Acad. Sci. Amsterdam*, **44**, 1045, 1177 (1941); **45**, 9, 126 (1942).
3) J. H. Fessler and A. G. Ogston, *Trans. Faraday Soc.*, **47**, 667 (1951).
4) P. G. W. Hawksley, "Some Aspects of Fluid Flow", Paper 7, Edward Arnold, London (1951).
5) S. Uchida, *Reports of the Institute of Science and Technology, University of Tokyo*, **3**, 97 (1949); An outline by J. Happel, *Ind. Eng. Chem.*, **46**, 1194 (1954).

various equations have been proposed. However, it has been difficult to verify any such equations, because of concentration ambiguity due to particle solvation or lack of particle size uniformity in the experimental cases.

Therefore an experiment was performed on polystyrene latex of uniform spherical shape. The polystyrene latex, Dow Latex 580 G, has been studied with various methods and the size and shape of particles are well established[6]. Particles are perfectly spherical and the diameter of particles is uniform within a small range. It was also shown that polystyrene particles are not hydrated to any observable amount[7], and the volume of the latex particle can be used as its hydrodynamic volume.

Experimental

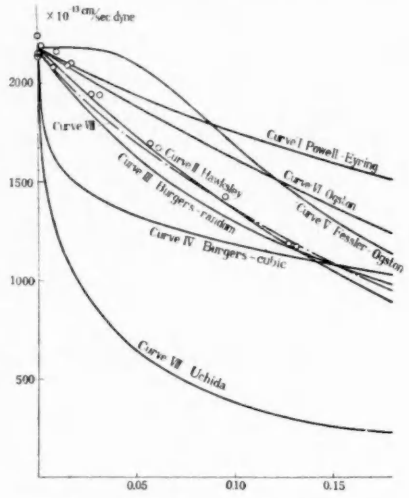
Materials and methods: By adding concentrated solution of sodium chloride, Dow Latex 580 G suspension was made 0.14 M in regard to sodium chloride, and then it was diluted to various concentrations by adding suitable amounts of 0.14 M sodium chloride solution. The solution was centrifuged in an ordinary laboratory centrifuge in a field of about 1000×g. for five minutes in order to remove aggregates.

For the determination of the concentration of latex particles, a few drops of the solution were weighed with a micro-balance, gently dried over phosphorus pentoxide and weighed again. Since the concentration of sodium chloride was known, the volume fraction concentration of latex particles was calculated using the value[7,8] for the density of polystyrene latex.

Sedimentation experiments were performed with an air-driven centrifuge of Pickels type[9] at a speed of 9000 r.p.m. The centrifugal field was about 6000 times that of gravity. The speed was controlled manually by changing the driving air pressure while observing a Lissajou's figure on a cathode ray oscillograph. The Lissajou's figure was formed by the potential caused by a magnet fixed on the air turbine, and the frequency of power supply was used as the reference. By this method the speed of rotation was readily kept within an error of 0.5%. The frequency of power supply was checked with a frequency meter.

The sedimenting boundary was observed and photographed through a schlieren optical apparatus. However, since polystyrene latex suspension was very opaque at all concentrations used in the experiment, we actually measured the absorption edge of the sedimenting boundary. The light source was a high pressure mercury discharge lamp, and was very intense. The exposure time was three seconds.

Results: sedimentation coefficients calculated and reduced for water at 20°C are shown in Fig. 1. Density and viscosity of solvent was used for the calculation. When the curve through measured points in Fig. 1 was extrapolated to zero concentration, a sedimentation coefficient of 2180 S was obtained.



Volume fraction concentration ϕ

Fig. 1. Sedimentation coefficient for polystyrene latex particles.

Discussion

The value of the sedimentation coefficient for Dow Latex 580 G at infinite dilution obtained above agrees well with the value obtained by Hogeboom and Kuff[10]. The work of Cheng and Schachman[11] was published after our completion of the experiment, and their value agrees well with the value obtained here when it is corrected for the temperature difference.

By using Stokes' law, the diameter of the polystyrene latex was calculated as 268 mμ from the sedimentation coefficient value extrapolated to infinite dilution. This is in good agreement with values obtained by other methods[6,12,13].

6) C. H. Gerould, *J. Appl. Phys.*, **21**, 183 (1950).
7) D. G. Sharp and J. W. Beard, *J. Biol. Chem.*, **185**, 247 (1950).
8) R. C. Williams and R. C. Backus, *J. Am. Chem. Soc.*, **71**, 4052 (1949).
9) I. Watanabe, Y. Kawade and S. Mizushima, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **73**, 828 (1952).
10) G. H. Hogeboom and E. L. Kuff, *J. Biol. Chem.*, **210**, 733 (1954).
11) P. Y. Cheng and H. K. Schachman, *J. Polymer Sci.*, **16**, 19 (1955).
12) W. B. Dandliker, *J. Am. Chem. Soc.*, **72**, 5110 (1950).
13) B. R. Leonard, Jr., J. W. Anderegg, P. Kaseberg and W. W. Beeman, *J. Appl. Phys.*, **23**, 152 (1952).

In Fig. 1, together with the experimental values, curves are shown which were calculated from formulae which have been proposed by various authors.

Curve I was calculated using the formula of Powell and Eyring[1].

$$s=s_0/(1+\nu\phi) \quad (1)$$

ϕ: Volume fraction concentration.
s: Sedimentation coefficient at ϕ.
s_0: Sedimentation coefficient at infinite dilution.
ν: Volume fraction limiting viscosity number for solute particles.

This formula was calculated by using a model in which only one particle was assumed to be sedimenting while all the other particles were assumed not to be in motion. However, such a situation is never realized in actual cases, as all the particles sediment at the same time. The fact that curve I does not agree with experimental points shows that the model used by Powell and Eyring was not suitable. It has also been pointed out[14] that in cases in which ν was very large, the term $(1+\nu\phi)$ of formula (1) was too large to explain experimental values.

Curve II in Fig. 1 was obtained from the formula of Hawksley[4],

$$s/s_0=(1-\phi)^2\exp.(-k\phi/(1-Q\phi)) \quad (2)$$

k: Einstein's shape factor for viscosity. 2.5 for spheres.
Q: Vand's interaction constant. 39/54 for spheres.

and is quite well fitted to the experimental values. This formula was derived by considering three effects: apparent increase of the viscosity of the medium by the presence of particles, apparent increase of buoyancy due to apparent increase of the density of the medium, and the back flow of the medium. However, when we consider the fact that all the particles sediment at the same time and there is no relative velocity between particles, the first and the second effect are not likely to exist. Hawksley calculated the first effect according to Vand's modification[15] of Einstein's formula for viscosity.

$$\eta_{rel.}=\exp.(k\phi/(1-Q\phi)) \quad (3)$$

$\eta_{rel.}$: Viscosity ratio.

However, it was reported by Cheng and Schachman[11] that formula (3) does not agree with experimental values for Dow Latex 580 G. If actual values[11] of the viscosity of the suspension of Dow Latex 580 G were substituted into formula (2), the sedimentation velocity at a concentration of 8% will be about 5% lower. Thus, the excellent coincidence of the values calculated by the formula (2) with experimental values seems to be fortuitous.

Burgers derived a relation for the dependence of sedimentation velocity on concentration assuming a hypothetical function of flow[2]. Curve III and IV show results obtained by Burgers. Curve III was calculated assuming a random arrangement of sedimenting particles and curve IV was calculated by assuming a cubic arrangement of particles. Curve III follows the experimental points fairly well.

The formula of Fessler and Ogston[3] is shown in Fig. 1 as curve V. This formula was derived by considering that when the concentration is very high the resistance of sedimenting particles approaches that of a porous plug, but is unsatisfactory in two points. The equation by Sullivan ane Hertel[16] for fluid flow through a porous plug is used in the formula, and it includes the effect of back flow of the medium by the nature of the equation. The use of the Enoksson's factor[17] in the derivation of the formula was theoretically unnecessary. It is also not justifiable to add the term $1/s_0$ to the term derived from the equation by Sullivan and Hertel. Recently Ogston[18] has used a modified form, and it is shown as curve VI in Fig. 1.

Curve VII shows the result numerically calculated by Uchida[5] on a model of spheres sedimenting in a cubic arrangement. The resistance calculated by using such a model is far larger than that for actual sedimenting latex particles, and this fact suggests that the actual arrangement shows less resistance than a cubic arrangement although particles are likely to be in some kind of arrangement while sedimenting. When particles are distributed at random in space and time, the average resistance against sedimenting particles should be, as was pointed out by Hawksley[4], inversely proportional to the volume fraction of the suspending medium. The increase of resistance due to this effect is too small to explain the

14) I. Jullander, *J. Polymer Sci.*, **2**, 329 (1947).
15) V. Vand, *J. Phys. Coll. Chem.*, **52**, 277 (1948).
16) R. R. Sullivan and K. L. Hertel, *Advances in Colloid Sci.*, **1**, 37 (1942).
17) B. Enoksson, *Nature*, **161**, 934 (1948).
18) A.G. Ogston, *Trans. Faraday Soc.*, **49**, 1481 (1953).

TABLE I

APPARENT VOLUME FOR MOLECULES WITH SOLVATION CALCULATED FROM THE CONCENTRATION DEPENDENCE OF SEDIMENTATION COEFFICIENT

Substance	v/v_0	$\sqrt[3]{v/v_0}$	f/f_0	$(f/f_0)/\sqrt[3]{v/v_0}$
Collagen[19]	8.5×10	4.4	9.7*	2.2
Herring sperm deoxyribonucleic acid. (Preparation Ib)[20]	6.4×10	4.0	5.0	1.25
Cellulose acetate[21] (in acetone)	4.3×10	3.5	3.5	1.0
Cellulose nitrate (Fraction I/6)[22] (in acetone)	3.0×10	3.1	4.6	1.5
Sodium cellulose xanthate[23] (Preparation No. 8)	2.0×10	2.7	3.4	1.3
Polystyrene (Fraction PSAF)[24] (in decaline)	1.4×10	2.4	3.3	1.3
Bovine serum albumin[25]	2.2	1.3	1.3	1.0
Calf thymus histone[26] (Histone I)	3.4	1.5	1.9	1.3
Bovine fibrinogen[27]				
Native	4.9	1.7	2.2	1.3
Denatured, at pH 5.5	1.2×10	2.3	3.0	1.3
Denatured, at pH 3.5	2.2×10	2.8	3.0	1.1

concentration dependence of the sedimentation coefficient, and suggests that the particles are in some kind of spacial arrangement with each other.

Curve VIII was drawn according to the formula*:

$$s_0=s\{1+\phi^{2/3}/(1-\phi^{1/3})^2(1+2\phi^{1/3})\} \qquad (4)$$

Within the range of concentration in which experiments were possible with polystyrene latex, formula (4) agreed well with the experimental points. Therefore formula (4) can be used as an experimental formula for the concentration dependence of the sedimentation coefficient.

Since the relation of sedimentation coefficient to concentration was experimentally established, and can be represented by formula (4), we came to be able to find the apparent volume of particles by measuring the concentration dependence of the sedimentation coefficient. The apparent volume obtained in such a way may be different from that for the substance in dry condition. The ratio of such apparent volume to the dry volume, v/v_0, was calculated for various substances from available values of sedimentation experiments and the results are shown in Table I. In all cases the curves for the dependence of sedimentation coefficient were very similar to that for the polystyrene latex, when s/s_0 values were plotted against volume fraction concentration calculated from the apparent volume in solution. This fact seems to suggest that the particles with solvation are nearly spherical in sphape in these cases. In the fourth column of Table I, values of the frictional ratio of particles calculated from values of the sedimentation coefficient and diffusion constant are shown. The cube root of v/v_0 and the frictional ratio have a very close relation with each other. This suggests that values of the frictional ratio larger than unity can be explained for the most part by the increase of

* When the concentration is high and each sphere is sedimenting surrounded by many other spheres of the same size at close distances, we may assume that at the middle point of a line which connects the center of the sphere to the center of one of the surrounding spheres, the line of flow is at a right angle to the line. Such a condition may be represented by a model in which a sphere moves at the center of a spherical shell on the surface of which the liquid slips perfectly. A simple calculation was performed on such a model using the Stokes' function of flow, and the resistance against the movement of the sphere was calculated. Then the sedimentation velocity of the sphere at the center of such a spherical shell was calculated as follows:

$$s=s_0(1-a/b)^2(1+2a/b)$$

where a is the radius of the sphere and b is the radius of the spherical shell. Thus a/b is approximately $\phi^{1/3}$. This model was too crude, and the calculated result did not agree with experimental results.

* This value is different from the value reported in the article cited. By later experiments the diffusion constant for collagen was found to be 0.3×10^{-7}cm^2./sec.

19) H. Noda, *Biochim. Biophys. Acta*, **17**, 92 (1955).
20) Y. Kawade, ibid., **19**, 513 (1957).
21) S. J. Singer, *J. Chem. Phys.*, **15**, 341 (1947).
22) H. Mosiman, *Helv. chim. Acta*, **26**, 61 (1943).
23) N. Gralen, Inaugural Dissertation, Uppsala 1944.
24) A. F. Schick and S. J. Singer, *J. Phys. Coll. Chem.*, **54**, 1028 (1950).
25) V. L. Konig and J. D. Perrings, *Arch. Biochem. Biophys.*, **41**, 367 (1952).
26) N. Ui in Press, This Bulletin.
27) H. A. Scheraga, W. R. Carroll, L. F. Nims, E. Sutton, J. K. Buckus and J. M. Saunders, *J. Polymer Sci.*, **14**, 427 (1954).

apparent volume of molecules or particles by solvation. The great amount of solvent which accompanies molecules in the cases of collagen and a preparation of deoxyribonucleic acid is surprising, but if such molecules are considered to be composed of long chains and to be in the shape of a random coil, it is possible for them to be accompanied by such an amount of solvent.

When the above method of estimating the amount of solvation was applied to the sedimentation data of fibrinogen by Scheraga et. al.[27], as is shown in Table I, the amount of solvation obtained for denatured fibrinogen was larger than that for native fibrinogen, and the increase in the frictional ratio due to denaturation was explained by the increase in the apparent volume of molecules. Scheraga et. al. reached a similar conclusion using their data on various hydrodynamic properties on the basis of the work of Scheraga and Mandelkern[28].

It should be noted that formula (4) was verified only for the case of sedimenting spheres. Therefore the above discussion is not decisive, especially in cases in which the ratio $(f/f_0)/\sqrt[3]{v/v_0}$ is far from unity. In order to determine exact contributions by the molecular shape and solvation to the increase of frictional ratio, we should know the relation between the molecular shape and the concentration dependence of the sedimentation coefficient.

28) H. A. Scheraga and L. Mandelkern, *J. Am. Chem. Soc.*, **75**, 179 (1953).

Summary

Experiments were performed in order to find out the relation between the volume fraction concentration and the sedimentation coefficient in a suspension of spheres. The polystyrene latex suspension, Dow Latex 580 G, was used as the suspension of spheres of known hydrodynamic properties. No theoretical equation proposed in the past corresponds well with the experimental result obtained here. Therefore an experimental equation,

$$s_0=s\{1+\phi^{2/3}/(1-\phi^{1/3})^2(1+2\phi^{1/3})\}$$

is proposed. Using this equation the amount of solvation in solution of some proteins and other molecules was calculated. The amount of solvation found is nearly enough to explain the frictional ratio for such molecules..

We should like to express our deep gratitude to Dr. Backus of the University of California who kindly provided us with Dow Latex 580 G suspension. The author is indebted to Dr. Yoshimi Kawade of the Virus Research Institute, Kyoto University for his cooperation in performing the sedimentation experiments and for his helpful discussions.

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The Stretching Vibration of N-H Link of 2-Aminopyridine

By Reisuke SODA

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Introduction

The Watson-Crick model on the molecular structure of deoxyribonucleic acid[1] has been regarded as an excellent picture but it leaves some doubts about its certainty. One of them is concerned with the tautomerism of base. The present study is undertaken in order to provide confirmatory data for the tautomerism of 2-aminopyridine as the simplest base.

Whether 2-aminopyridine exists in the amino form or in the imino form has been discussed for years[2-4] and now many

1) J. D. Watson and F. H. C. Crick, *Nature*, **171**, 737, 964 (1953); F. H. C. Crick and J. D. Watson, *Proc Roy. Soc., London*, **A223**, 80 (1954).

2) E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948); L. C. Anderson and N. V. Seeger, ibid., **71**, 340 (1949).

3) A. E. Tschitschibabin, R. A. Konowalowa and A. A. Konowalowa, *Chem. Ber.*, **54B**, 814 (1951).

4) S. L. Angyal and C. L. Angyal, *J. Chem. Soc.*, **1952**, 1461.

results support the amino form of this compound. Experimental results obtained from infrared absorption spectra[5,6] also support the amino form but their discussions are limited on the absorption band position of the stretching vibration and the deformation vibration of the N-H link; consequently their conclusions appear to be qualitative and unsatisfactory. In this report the observation covers not only the band frequency but also the integrated intensity; moreover a reliable conclusion for the amino form is obtained.

Experimental

The Perkin-Elmer model 112 spectrophotometer with a lithium fluoride prism was used[7], but the measurement on toluidines was carried out with a calcium fluorite prism. The theoretically calculated slit widths were 5 cm.$^{-1}$ at 3400 cm.$^{-1}$ for the calcium fluorite and 3 cm.$^{-1}$ for the lithium fluoride. These values were about one fifth of each band width, but the actual slit widths were considered to be wider than the aforementioned values[5]. The cell thickness was about 10 mm. and the concentration of solution was taken from 0.02 moles per liter to 0.001, in order to put optical densities in the range of 0.8 to 0.2. The range of the observed wave number was from 3700 cm.$^{-1}$ to 3000 cm^{-1}.

The c.p. carbon tetrachloride was used as the solvent, which was distilled after drying with phosphorous pentoxide. The reagents were purified as follows. Aniline was distilled at 90°C/16 mmHg and pyrrole at 130°C. Indole[9] was recrystallized from ethanol-water solvent. 2-Aminopyridine was recrystallized from ligroine with petroleum ether, one part of which was further purified by vacuum distillation. Only c.p. toluidines were used without purification.

N-Methyl-2-pyridonimine was synthesized from methyl iodide and 2-aminopyridine by the method of Tschitschibabin et al.[8]; after recrystallization of the product, 2-aminopyridine methiodide from alcohol, its aqueous solution was treated with fresh silver oxide obtained from silver nitrate and sodium hydroxide and the filtrate was concentrated *in vacuo*. The final viscous greenish liquor was distilled at 100°C/12 mmHg. The distillate was slightly yellow and viscous, and turned to a brownish-red substance which became more viscous in the air. Therefore the distillation was carried out at every measuremnt. The purities of reagents were justified by comparison of observed spectra with those given in the literatures.

The molar extinction coefficient and the integrated intensity of the absorption band were obtained with the usual extrapolation method[5]. But in the case of a band overlapping, the following method is preferable. First, the total area of two bands is measured with planimeter. Next, the values of the products, 'the peak optical density times the half-band width' for both the absorption bands are obtained respectively and the ratio of these values is calculated. Then the total area is proportionally divided into two bands according to this ratio and the area of each band determined.

The units of those values are as follows:

$$E=(1/cl)\log_{10}(I_0/I)\,\text{cm.}^2\cdot\text{mol.}^{-1}$$

$$A=(1/cl)\int\ln(I_0/I)\,d\nu\,\text{cm.}^2\cdot\text{molecule}^{-1}\cdot\text{sec.}^{-1}$$

Where c is the concentration of the solution in moles per cc. for the molar extinction coefficient E, and in number of molecules per cc. for the integrated intensity A; l, the thickness of the cell in cm.; ν, the frequency of the infrared rays in cycles per sec,; I_0 and I, the radiation intensity transmitted through the solvent and solution respectively.

Results

In the Table, the peak frequency (the band position) ν, the molar extinction coefficient E, the half-band width $\Delta\nu_{1/2}$, and the integrated intensity A are cited. Aniline and three isomers of toluidines, which are representatives of the compounds of the amino form, give rise to two absorption bands near 3480 cm.$^{-1}$ and 3390 cm.$^{-1}$, those bands having the intensities of the same order. The spectrum of 2-aminopyridine shows a similar tendency as the aforementioned four compounds. The heterocyclic compounds as pyrrole and indole, in which a hydrogen atom links to the ring nitrogen atom, show the spectra

TABLE I
OBSERVED VALUES OF THE N-H STRETCHING VIBRATIONS

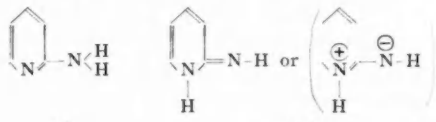
Compounds	ν (cm.$^{-1}$)	$E\times10^{-4}$ (cm.^{2} mol.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$A\times10^{-5}$ (cm.^{2} molecule^{-1} sec.$^{-1}$)
Pyrrole	3495	25	13	65
Indole	3490	23	13	60
N-Methyl-2-pyridonimine	3322	1.8	24	9
2-Aminopyridine	3510	5.4	32	28
	3410	7.6	25	31
Aniline	3481	3.0	39	17
	3397	3.8	28	15
o-Toluidine*	3481	3.1	35	15
	3399	3.5	26	12
m-Toluidine*	3479	3.1	39	18
	3396	3.9	28	16
p-Toluidine*	3472	2.9	39	17
	3391	3.6	29	16

* The data of toluidines are obtained with a calcium fluoride prism, whilst others with a lithium fluoride prism.

5) C. L. Angyal and R. L. Werner, ibid., 2911.
6) J. D. S. Goulden, ibid., 2939.
7) The measurement was carried out in the Laboratory of Professor Kunio Kozima in Tokyo Institute of Technology, Tokyo.
8) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
9) This sample was kindly given by Mr. Takaaki Tamura, in this Institute.

with one sharp and intense absorption band attributed to the stretching vibration of the N-H link near 3490 cm.$^{-1}$. The spectrum of N-methyl-2-pyridonimine[10] which is selected as a representative of the compound of the imino form, shows a weak and broad band at 3322 cm^{-1}.

The above results are obtained from the measurements in a fairly dilute solution and there seems no absorption band which is ascribed to the associated molecule. From the data of the other authors[11] it can be also said that there will be no fear of the existence of the associated molecule in such a low concentration.



(a) (b)

Fig. 1. The tautomerism of 2-aminopyridine.

Discussion

As illustrated in the Table, the compounds of the amino form generally show two absorption bands with the same order of intensities near 3480 cm.$^{-1}$ and 3390cm^{-1}. Of these bands, the higher frequency one is assigned to the antisymmetric and the lower to the symmetric vibration of the NH_2 group, and the integrated intensity of the former is somewhat larger than the latter. While in 2-aminopyridine two bands are observed at 3510 cm.$^{-1}$ and 3410 cm.$^{-1}$ respectively and the integrated intensity of the former has larger value than the latter, the values of which are considerably larger than those of aniline etc. Although there are such trivial differences from aniline etc., the facts that the bands appear at the similar positions as aniline etc. and that intensities of the two bands have the values of the same order, show the coincidence of the spectrum of 2-aminopyridine with those of the compound of the amino form[12].

If 2-aminopyridine exists in the imino form, (Fig. 1b), then the absorption spectrum will show approximately the sum of the absorption assigned to the vibrations of the N-H link of pyrrole type and that of imino type; i.e., a sharp and strong band near 3490 cm.$^{-1}$ and a broad and extraordinarily weak band near 3320 cm^{-1}. This feature does not even qualitatively coincide with the observed spectrum of 2-aminopyridine. In fact, in the spectrum of 2-aminopyridine, there is no band near 3320 cm.$^{-1}$ and even if for some reasons this band would shift to about 3410 cm^{-1}., it will be impossible to explain the fact that the value of the integrated intensity of the band of the lower frequency vibration is apparently larger.

From those facts it will be concluded that 2-aminopyridine exists mainly or decidedly in the amino form in a dilute solution of the nonpolar solvent.

In the spectrum of 2-aminopyridine, a wing of the band of 3410 cm^{-1}. extends to 3320 cm^{-1}. but no superposition of bands is observed. If the tautomerism exists between the imino and the amino form (Fig. 1), considering the experimental accuracy and the noise level of spectrum, it is possible to estimate the ratio of the number of the molecules of imino structure allowed to exist to that of the amino structure. According to the simple calculation this possibility is estimated to be less than 0.5 %, hence even if there were a tautomerism it is concluded that the amino form is decidedly predominant over the imino form. This conclusion is consistent with the measurement on the pK_a, in which such a possibility is estimated to be less than 0.001 %[1].

Summary

The infrared absorption spectrum of 2-aminopyridine was observed and compared with those of other compounds and the amino form of 2-aminopyridine was confirmed. The imino form was rejected and even if this tautomeric form exists its quantity is estimated to be negligibly small.

The author wishes to express his hearty thanks to Assistant Professor Kenji Kuratani for his kind guidance and encouragement throughout this work. The author is indebted to Mr. Kiyoshi Sakashita in the Laboratory of Professor Kunio Kozima for his kind help at the time of the measurement of the infrared absorption spectra.

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10) N-Methyl-2-pyridonimine is very hygroscopic and even its dilute solution is not sufficiently transparent, but there is almost no influence of such a property on the observation.

11) N. Fuson, M-L. Josien, R. L. Powell and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952).

12) For the considerable increment of the intensity of 2-aminopyridine, the following qualitative explanation is given. Generally when the electrophilic radical or atom combines to the ring, the band shifts to the higher frequency[6] and the ionic character of NH bond is considered to increase, so that the change of the dipole moment in the vibration will become larger.

Absorption Spectra of Heteropolyanions. II[1] *The Heteropolytungstates Containing Co(II), Co(III) or Mn(IV) as Central Ions*

By Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received February 18, 1957)

Introduction

In the former paper of this series[1], the absorption spectra were reported for the heteropolymolybdates containing Co(III), Cr(III), Fe(III), Al(III), Mn(IV) or Ni(IV) as central ions. X-ray investigations[2,3], magnetic measurements[4] and other physico-chemical studies[5] by many authors have revealed that the central ion M is at the center of MO_6 octahedron. The absorption spectra of these heteropolymolybdates were therefore regarded as the absorption spectra of $[M(O^{=})_6]$-complexes.

In the present paper, absorption spectra of the heteropolytungstates containing some transition metals as central ions have been measured. Of special interest are the heteropolyanions containing Co (II) or Co(III), which were very recently discovered and thoroughly investigated by Baker and McCutcheon[6]. Our spectral studies have clearly established the fact that the Co(II) or Co(III) ion is at the center of a tetrahedron, in contrast to the conclusion of Baker et al., who offered some octahedral structures.

The present paper is probably the first one that describes the absorption spectra of $[Co^{II}(O^{=})_4]$- and $[Co^{III}(O^{=})_4]$-complexes.

Experimental

The absorption measurements were made in aqueous solutions by a Beckman DU spectrophotometer at room temperature. The concentration of the solutions varied from 0.5×10^{-2} to 0.2×10^{-4} F/l. The formula weights were calculated from the formulae listed in Table I, on which are also tabulated the literature for preparation and the tentative structural formulae which are proposed for the anions from our spectral studies.

Results and Discussion

(1) $3Na_2O\cdot5WO_3\cdot Mn^{IV}O_2\cdot18H_2O$—The absorption spectrum of this compound is shown in Fig. 1, in which the spectrum[1] of $[Mn^{IV}O_6Mo_9O_{26}]^{6-}$ is also plotted for

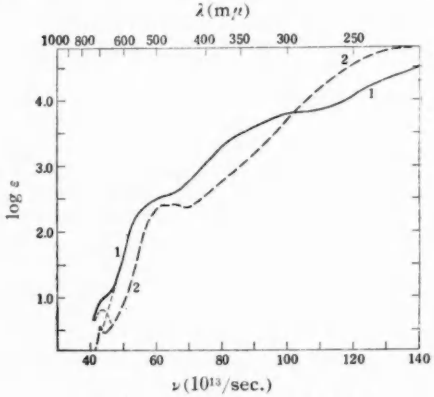

Fig. 1. Absorption spectra of:
1, $3Na_2O\cdot5WO_3\cdot Mn^{IV}O_2\cdot18H_2O$;
2, $(NH_4)_6[Mn^{IV}O_6Mo_9O_{26}]\cdot6H_2O$[1].

comparison. The structure of the latter ion was well established by an X-ray analysis[2]. Therefore, a broad band at 64.1×10^{13}/sec. ($\log\varepsilon_{max}=2.42$) and a narrow band at 42.9 (0.55), are equally due to the complex $[Mn^{IV}(O^{=})_6]$. Recently, from the viewpoint of crystal field theory, Jørgensen[8] suggested that the narrow band is due to a spin-forbidden transition $^4T'_2\leftarrow{}^2T'_3$ and the broad band to a spin-allowed transition $^4T'_2\leftarrow{}^4T'_5(F)$.

As to the heteropolytungstate presently studied, the narrow band is observed as an inflation of the absorption curve. A curve analysis shown in Fig. 1 as dotted lines, gives the maximum intensity log ε=ca. 0.8 at frequency ca. 43.5. The broad band is similar to that of the correspond-

1) Part I of this series: Y. Shimura, H. Ito and R. Tsuchida, *J. Chem. Soc. Japan*, **75**, 560 (1954).
2) J. L. T. Waugh, D. P. Shomaker and L. Pauling, *Acta Cryst.*, **7**,438 (1954).
3) C. W. Wolfe, M. L. Block and L. C. W. Baker, *J. Am. Chem. Soc.*, **77**, 2200 (1955).
4) P. Ray, A. Bhaduri and B. Sarma, *J. Indian Chem. Soc.*, **25**, 51 (1948).
5) L. C. W. Baker, G. Foster, W. Tan, F. Scholnick and T. P. McCutcheon, *J. Am. Chem. Soc.*, **77**, 2136 (1955).
6) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).
7) A. Just, *Ber.*, **36**, 3619 (1903).
8) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

TABLE I

FORMULAE OF THE HETEROPOLYTUNGSTATES

Formula previously used	Formula Weight	Color	Literature for preparation	Tentative structural formulae for the heteropoly-anions
$3Na_2O \cdot 5WO_3 \cdot Mn^{IV}O_2 \cdot 18H_2O$	1756.5	orange red	7)	$[(Mn^{IV}O_6W_5O_{14})_n]^{6n-}$
$K_5H_5[Co^{II}(W_2O_7)_6] \cdot 16H_2O$	3426.1	bluish green	6)	$[Co^{III}O_4W_{12}O_{38}]^{10-}$ or $[Co^{III}O_4W_{12}O_{36}]^{6-}$
$K_4H_5[Co^{III}(W_2O_7)_6] \cdot 18H_2O$	3423.0	golden yellow	6)	$[Co^{III}O_4W_{12}O_{38}]^{9-}$ or $[Co^{III}O_4W_{12}O_{36}]^{5-}$
$(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})] \cdot 20H_2O$	3501.3	emerald green	6)	$[Co^{II}O_4(W_{12}O_{32})O_6Co^{II}]^{8-}$
$K_7[Co^{II}Co^{III}(W_{12}O_{42})] \cdot 16H_2O$	3558.2	dark brown	6)	$[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$

ing molybdenum compound, i.e., maximum at about 63 with intensity log ε_{max}=ca. 2.5.

Another very broad band is situated at the frequency region of 70–100. This is probably due to a polynuclear structure,

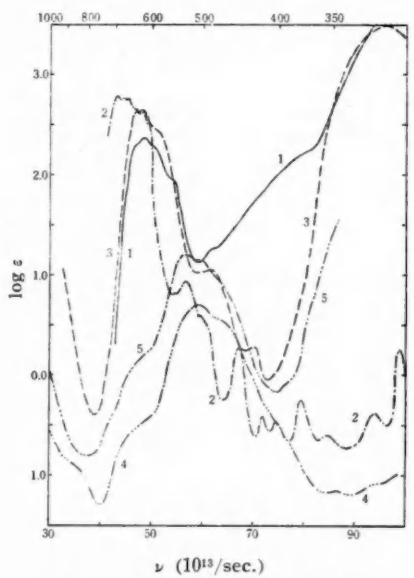

Fig. 2. Absorption spectra of:
1, $K_5H_5[Co^{II}(W_2O_7)_6] \cdot 16H_2O$;
2, $[Co\ Cl_4]^{2-}$ [11];
3, $[Co\ (NCS)_4]^{2-}$ [12];
4, $[Co\ (OH_2)_6]^{2+}$ [13];
5, $[Co\ (ox)_2\ (OH_2)_2]^{2-}$ [14].

i.e., a structure having two or more central manganese(IV) atoms with a linkage of Mn-O-Mn in the anion. A similar conclusion was previously obtained by the present authors[1] in connection with a heteropolymolybdate, $2(NH_4)_2O \cdot Co^{III}_2O_3 \cdot 10MoO_3 \cdot 12H_2O$, in which the ratio of central hetero-atom to molybdenum atom is 1 : 5. Likewise in the heteropoly tungstate concerned, the ratio of Mn : W is 1 : 5.

In conclusion, a tentative structural formula $[(Mn^{IV}O_6W_5O_{14})_n]^{6n-}$ may be assigned to the anion of this salt.

(2) $K_5H_5[Co^{II}(W_2O_7)_6] \cdot 16H_2O$—In Fig. 2, the absorption spectrum of this compound is compared with those of some cobalt (II) complexes, the structure of which was well established. $[CoCl_4]^{2-}$ and $[Co\ (NCS)_4]^{2-}$ are tetrahedral and have very different spectra in visible region as compared with those of octahedrally co-ordinated cobalt (II) complexes such as $[Co(OH_2)_6]^{2}$ etc.[12,15,16] From the figure, it is evident that the heteropolytungstate has a tetrahedrally co-ordinated cobalt (II) ion. The spectrochemical series for ligands of tetrahedrally co-ordinated cobalt (II) complexes have now been determined as follows:

O^{-} (heteropolytungstate)*, NCS^{-}, Cl^{-}, Br^{-} [17], I^{-} [17].

The order coincides very well with that of cobalt (III) complexes[9,10]. Baker et al.[6] assigned to this heteropolyanion a structural formula $[Co^{II}O_6W_{12}O_{36}]^{10-}$. But some modifications seem necessary on the basis of the above spectral data. The anion is probably represented by the formula $[Co^{II}O_4W_{12}O_{38}]^{10-}$ or $[Co^{II}O_4W_{12}O_{36}]^{6-}$.

(3) $K_4H_5[Co^{III}(W_2O_7)_6] \cdot 18H_2O$—This is a cobalt (III) analogue of the cobalt (II)

* Maximum values: ν_{max}=48.4×10¹³/sec., log ε_{max}=2.36.

9) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).
10) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).
11) A. Kiss and M. Gerendás, *Z. Physik. Chem.*, **A180**, 117 (1937).
12) S. Yamada and R. Tsuchida, This Bulletin, **27**, 436 (1954).
13) H. Ito, *J. Chem. Soc. Japan*, **77**, 1383 (1956).
14) H. Ito, unpublished data.
15) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).
16) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).
17) W. R. Brode, *J. Am. Chem. Soc.*, **53**, 2457 (1931).

compound above mentioned. The two species can be reversibly converted into each other by oxidation and reduction[6]. This fact suggests that the central cobalt (III) atom in the oxidized species is also surrounded by four oxigen atoms. As was expected from this, the spectrum of this compound has a very unique feature and is entirely different from the spectra of hexa-coordinated Co (III) complexes (Fig. 3). A broad maximum is observed at frequency of about 77.0 with intensity $\log \varepsilon = 3.10$. This is the first example of

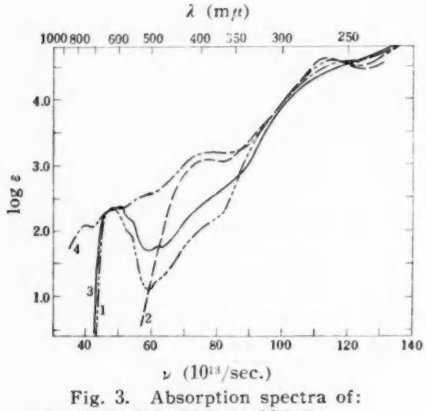

Fig. 3. Absorption spectra of:
1, $K_5H_5[Co^{II}(W_2O_7)_6]\cdot 16H_2O$;
2, $K_8H_5[Co^{III}(W_2O_7)_6]\cdot 18H_2O$;
3, $(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})]\cdot 20H_2O$;
4, $K_7[Co^{II}Co^{III}(W_{12}O_{42})]\cdot 16H_2O$.

such a tetrahedrally co-ordinated cobalt (III) complex, of which the spectrum was measured. A heteropolymolybdate containing a hexa-coordinated Co (III) atom shows in this region two absorption bands with lower intensities[1].

(4) $(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})]\cdot 20H_2O$ — The absorption spectrum of this compound (Fig. 3) reveals that it contains at least one cobalt(II) atom in tetrahedrally co-ordinated state. The intensity of the band characteristic of the tetrahedral cobalt(II) ion is of the same order of the uninuclear cobalt(II) heteropolytungstate above mentioned. Thus it is perhaps certain that the other cobalt(II) atom in this compound has an octahedrally co-ordinated structure. Since such an octahedrally co-ordinated cobalt(II) ion is expected to have less intense absorption than a tetrahedral cobalt(II) ion, the presence of the octahedral cobalt(II) ion has little contribution to the total form of the absorption curve. A tentative structural formula $[Co^{II}O_4(W_{12}O_{32})O_6Co^{II}]^{8-}$ seems adequate for the anion. This is in good agreement with the chemical evidence reported by Baker et al.[6] who concluded that the two cobalt atoms are structurally non-equivalent.

(5) $K_7[Co^{II}Co^{III}(W_{12}O_{42})]\cdot 16H_2O$ — This dark brown compound can be reversibly converted into the above mentioned $Co^{II}Co^{II}$ compound. The absorption curve of the compound has a complicated structure as is seen in Figs. 3 and 4. The occurrence of a broad band at about 78.0 ($\log \varepsilon_{max} = 3.20$) proves that the cobalt atom which was oxidized is the tetrahedrally co-ordinated one. Therefore the formula of this anion becomes $[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$.

The complicated bands in the visible region suggest the interactions between the

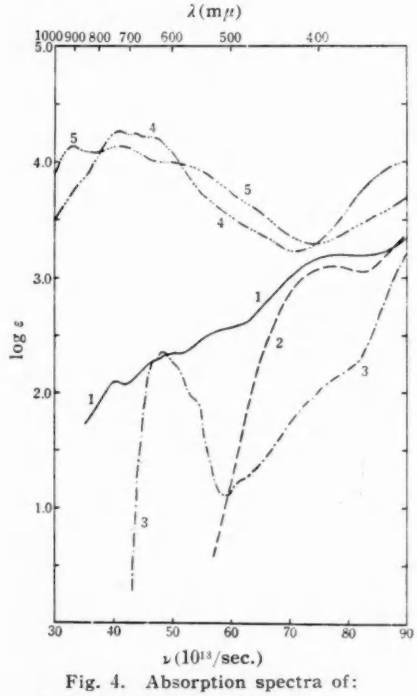

Fig. 4. Absorption spectra of:
1, $[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$;
2, $[Co^{III}O_4(W_{12}O_{34})]^{9-}$ or $[Co^{III}O_4(W_{12}O_{36})]^{5-}$;
3, $[Co^{II}O_4(W_{12}O_{34})]^{10-}$ or $[Co^{II}O_4(W_{12}O_{36})]^{6-}$;
4, $+4e^-$ reduction product of $H_4[SiO_4Mo_{12}O_{36}]$[18];
5, $+5e^-$ reduction product of $H_4[SiO_4Mo_{12}O_{36}]$[18].

18) J. D. H. Strickland, *J. Am Chem. Soc.*, **74**, 862 (1952).

cobalt atoms in different oxidation states. For this anion, Baker et al.[6] assigned the structure wherein given WO_6 octahedra are simultaneously attached to two central cobalt atoms. If this is the case, the interactions between the two cobalt atoms must occur through the bridged —O—W—O— group. If an electron-transfer-process is considered, this interaction will be represented as follows:

$$Co^{3+}—O—W^{6+}—O—Co^{2+}$$
$$\rightleftharpoons Co^{3+}—O—W^{5+}—O—Co^{3+}$$
$$\rightleftharpoons Co^{2+}—O—W^{6+}—O—Co^{3+}.$$

It is well known that the reduction products of tungstates or molybdates are colored intense deep blue. The absorption spectra of such reduction products of $H_4[SiO_4Mo_{12}O_{36}]$, which were thoroughly studied by Strickland[18], are reproduced in Fig. 4. The resemblance of these spectra with the visible spectrum of the $Co^{II}Co^{III}$ heterotungstate anion, except that the intensity of the latter compound is lower by a factor of about 10^2, will be regarded as a proof for the interaction of the above mentioned type.

(6) Absorption band originating in tungstate skeleton.—All of the heteropolytungstates herein studied have very broad and intense absorption bands in ultraviolet region. This is certainly the absorption due to the tungstate skeleton. Similar but more diffuse molybdate bands have been observed by the present authors[1] for the heteropolymolybdates previously reported.

Summary

The visible and ultraviolet absorption spectra have been measured for some heteropolytungstates containing cobalt(II), cobalt(III) or manganese(IV) as central ions.

It has been shown that some cobalt(II) or cobalt (III) ions in the heteropolytungstates have tetrahedral co-ordination. This is the first case of the absorption spectra of $[Co^{II}(O^{=})_4]$- and $[Co^{III}(O^{-})_4]$-complexes being measured.

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*Studies on Azeotropic Mixtures. III. Physical Basis of Azeotropic Correlation Rules**

By Toshio YOSHIMOTO

(Received February 8, 1957)

Introduction

Though several useful correlation rules of azeotropic data have been reported, they appear to lack in a common physical basis because the theory of azeotropes is little developed. It has been exemplified in part II[1] that the molecular interchange energy w for azeotropes composed of one common component (azeotropic reagent) and the members of a homologous series was constant in a number of cases, applying Trouton's rule to such a series. Also, the equations

$$\Delta_v S_1^0 (T_1^0 - T^a) = Nwx_2^2 \quad (1)$$

and

$$\Delta_v S_2^0 (T_2^0 - T^a) = Nwx_1^2 \quad (2)$$

derived in part I[2] have proved to be useful in predicting azeotropic data. Here, T^a is the azeotropic point (for $p=1$ atm.), N, the Avogadro number, $\Delta_v S_i^0$ the molar entropy of vaporization at boiling point T_i^0 (for $p=1$ atm.) of pure component ($i=1$ and 2), and x_1, x_2 mole fraction of both components respectively.

It will be shown in this paper that the equations (1) and (2) may give some information about the mutual relationship between independent correlation rules as well as their physical basis.

* Partly presented at the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956.

1) T. Yoshimoto and Y. Mashiko, This Bulletin, **30**, 56 (1957).

Relation between Boiling Points of Homologous Members and Azeotropic Composition

Now eliminating T^a between two equations (1) and (2), we have the following quadratic equation for x_2:

$$(S_2-S_1)x_2^2+2S_1x_2 - \left\{S_1+\frac{S_1S_2}{W}(T_1^0-T_2^0)\right\}=0^{**} \qquad (3)$$

This can be solved for x_2 to give

$$x_2=-\frac{S_1}{S_2-S_1} \pm \frac{\sqrt{S_1S_2}}{S_2-S_1}\left\{1+\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^{1/2}. \qquad (4)$$

The necessary and sufficient condition for azeotrope existence is

$$-\frac{W}{S_2}<T_1^0-T_2^0<\frac{W}{S_1}, \qquad (5)$$

as shown by us in part I and we see obviously $S_2-S_1<S_1$ in numerical values, so we can obtain readily

$$\left\{\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^2<1.$$

We may therefore develop (4) in convergent power series of $T_1^0-T_2^0$:

$$x_2=\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}+\frac{\sqrt{S_1S_2}}{2W}(T_1^0-T_2^0) +\frac{\sqrt{S_1S_2}(S_2-S_1)}{8W^2}(T_1^0-T_2^0)^2 +\frac{3\sqrt{S_1S_2}(S_2-S_1)^2}{48W^3}(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (6)$$

Here, component 2 is chosen as a common azeotropic reagent, that is usually a more "associated" liquid, and must have larger entropy of vaporization than component 1. Lecat[3] obtained empirically a series of equations in the form

$$C=C_0+C_1\Delta+C_2\Delta^2 \qquad (7)$$

where C is wt. % of the second component, Δ the difference between boiling points of pure component, i.e. $T_1^0-T_2^0$, and C_0, C_1 and C_2 are all constants for a given series of homologous azeotropes. The equation (6) will thus interpret Lecat's empirical rule despite the fact that his rule differs in composition scale of azeotrope. If for example, the numerical values given in part II[1] for the series of azeotropes between 1-butanethiol and paraffinic hydrocarbons are introduced into equation (6), i.e., $S_1=20.3$, $S_2=22.0$ and $W=280$, we obtain

$$x_2=0.49+0.038(T_1^0-T_2^0) +0.000057(T_1^0-T_2^0)^2 +0.00000017(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (8)$$

The coincidence of calculated curve with observed values is tested and the result shown in Fig. 1.

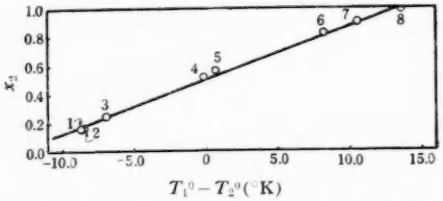

Fig. 1. Test of equation (8) for azeotropes of 1-butanethiol with paraffinic hydrocarbons: full line calculated, circles experimental. Paraffinic hydrocarbons: (1), 2, 3-Dimethylpentane; (2), 2-Methylhexane; (3) 3-Methylhexane; (4), *n*-Heptane; (5), 2,2,4-Trimethylpentane; (6), 2,2-Dimethylhexane; (7), 2,5-Dimethylhexane; (8), 3,3-Dimethylhexane.

Azeotropic data are taken from R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949).

Since the boiling-point difference between components in this case is less than 14°C as judged by the discussion of azeotrope-forming range presented in part II[1], we may neglect the third and higher order terms and therefore obtain approximately

$$x_2=\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}+\frac{\sqrt{S_1S_2}}{2W}(T_1^0-T_2^0). \qquad (9)$$

This will thus interpret the straight-line relationship between x_2 and T_1^0 proposed by Denyer et al[4]. The straight-line relationship is true in the azeotropes of organosulfur compounds such as thiol, sulfone, etc. with aliphatic hydrocarbons, where the difference between S_1 and S_2 is not so great.

In the limiting case where S_1 is equal to S_2, equation (6) reduces to

$$x_2=\frac{1}{2}\left\{1+\frac{S}{W}(T_1^0-T_2^0)\right\} \qquad (10)$$

and then we have

2) T. Yoshimoto and Y. Mashiko, This Bulletin, **29**, 990 (1956).

** Hereafter the S_i and the W refer, for brevity, to $\Delta_e S^0{}_i$ and Nw respectively.

3) L. H. Horsley, *Anal. Chem.*, **19**, 603 (1947).

4) R. L. Denyer, F. A. Fidler and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949); D. H. Desty and F. A. Fidler, ibid., **43**, 905 (1951).

$$x_1=\frac{1}{2}\left\{1-\frac{S}{W}(T_1^0-T_2^0)\right\}, \qquad (11)$$

where we write $S_1=S_2=S$ for brevity. The equations (10) and (11) are identical with those derived theoretically by Kuhn[5] for the azeotropes of dispersion force solutions where S_1 is approximately equal to S_2.

When T_1^0 is equal to T_2^0 in equation (9), we find

$$x_2=\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}<\frac{1}{2},$$

while x_2 is 1/2 in the limiting case where S_1 is equal to S_2.

Relation between Boiling Points of Homologous Members and Their Azeotropes with One Common Azeotropic Reagent

Another type of correlation is noticed in azeotropic data when we plot T^a against T_1^0. It has many advantages over the previous one especially in not needing any laborious analysis of azeotropic composition.

Eliminating x_1 and x_2 between two equations (1) and (2), we have a quadratic equation for $T_2^0-T^a$ in the form

$$\left(\frac{S_2}{W}-\frac{S_1}{W}\right)^2(T_2^0-T^a)^2+2\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)-\left(\frac{S_1}{W}+\frac{S_2}{W}\right)-\frac{S_1S_2}{W^2}(T_1^0-T_2^0)\right\}\times(T_2^0-T^a)+\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)-2\frac{S_1}{W}(T_1^0-T_2^0)+1\right\}=0. \qquad (12)$$

This can be solved for $T_2^0-T^a$ to give

$$T_2^0-T^a=\frac{-\left\{\frac{S_1^2}{W^2}(T_1^0-T_2^0)-\left(\frac{S_1}{W}+\frac{S_2}{W}\right)-\frac{S_1S_2}{W^2}(T_1^0-T_2^0)\right\}\pm\sqrt{4\frac{S_1S_2}{W^2}\left\{1+\left(\frac{S_2}{W}-\frac{S_1}{W}\right)(T_1^0-T_2^0)\right\}}}{\left(\frac{S_2}{W}-\frac{S_1}{W}\right)^2} \qquad (13)$$

Also noting that $\left\{\frac{S_2-S_1}{W}(T_1^0-T_2^0)\right\}^2<1$ and $S_2>S_1$, we may develop (13) in convergent power series of $T^0_1-T_2^0$:

$$T_2^0-T^a=\frac{W}{(\sqrt{S_1}+\sqrt{S_2})^2}-\frac{\sqrt{S_1S_2}-S_1}{S_2-S_1}(T_1^0-T_2^0)+\frac{\sqrt{S_1S_2}}{4W}(T_1^0-T_2^0)^2-\frac{\sqrt{S_1S_2}(S_2-S_1)}{8W^2}(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (14)$$

When the numerical values for the series of 1-butanethiol-paraffinic hydrocarbon azeotropes are, as before, introduced into (14), we obtain

$$T_2^0-T^a=3.31-0.49(T_1^0-T_2^0)+0.019(T_1^0-T_2^0)^2-0.000057(T_1^0-T_2^0)^3+\cdots\cdots. \qquad (15)$$

The coincidence of calculated curve with observed values is tested and the result shown in Fig. 2.

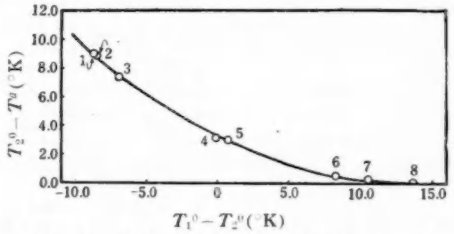

Fig. 2. Test of equation (15) for azeotropes of 1-butanethiol with paraffinic hydrocarbons: full line calculated, circles experimental.
Paraffinic hydrocarbons: see Fig. 1.

This will thus interpret Lecat's other empirical rule[6], i.e.,

$$\delta=A_0+A_1\Delta+A_2\Delta^2+A_3\Delta^3, \qquad (16)$$

where δ is the azeotropic depression $T_2^0-T^a$ and A_0, A_1, A_2 and A_3 are all constants for a given series of homologous azeotropes.†

†In the limiting case where S_1 is equal to S_2, we have from equation (14)

$$T_2^0-T^a=\frac{W}{4S}-\frac{1}{2}(T_1^0-T_2^0)+\frac{S}{4W}(T_1^0-T_2^0)^2. \qquad (17)$$

5) W. Kuhn and P. Massini, *Helv. Chim. Acta*, **33**, 737 (1950).

6) M. Lecat, *Z. anorg. allgem. Chem.*, **186**, 123 (1930); L. H. Horsley, *Anal. Chem.*, **19**, 603 (1947).
Similar explanation of this Lecat's rule was given by I. Prigogine and R. Defay, "Chemical Thermodynamics," Translated by D. H. Everett, Longmans (1954), p. 465.

This is identical with that derived by Kuhn[5] for dispersion force solutions if the third term is neglected, since it is not serious in such solutions.

The closer T_1^0 approaches T_2^0 in the equation (14), the more depression we have for azeotropic point and in the limit we have the maximum depression in the form

$$(T_2^0-T^a)^{\max}=\frac{W}{(\sqrt{S_1}+\sqrt{S_2})^2}, \qquad (18)$$

where the depression implies the difference in boiling point of azeotrope and the lower boiling component. The maximum depression is therefore regarded as a measure of azeotrope-forming power of the series.

Skolnik[7] proposed a different type of correlation between T^a and T_1^0 in the form

$$\log (D-T^a)=E-FT_1^0, \qquad (19)$$

where D is the asymptotic value and E and F constants. For dispersion force solutions such as azeotropes formed by toluene with naphthene homologues, D is approximately T_2^0. The equation (19) is thus modified into

$$T_2^0-T^a=Ae^{-B(T_1^0-T_2^0)}, \qquad (20)$$

where A and B are constants. If we assume

$$A=\frac{W}{4S}$$

and

$$B=\frac{2S}{W},$$

then we obtain

$$\begin{aligned} T_2^0-T^a &= \frac{W}{4S}\epsilon^{-\frac{2S}{W}(T_1^0-T_2^0)} \\ &= \frac{W}{4S}\left\{1-\frac{2S}{W}(T_1^0-T_2^0)\right. \\ &\quad \left.+\frac{2S^2}{W^2}(T_1^0-T_2^0)^2-\cdots\cdots\right\} \\ &= \frac{W}{4S}-\frac{1}{2}(T_1^0-T_2^0) \\ &\quad +\frac{S}{2W}(T_1^0-T_2^0)^2-\cdots\cdots. \qquad (21) \end{aligned}$$

By comparing (21) with (17) we have an information on the physical meaning of Skolnik's constants E and F.

7) H. Skolnik, *Ind. Eng. Chem.*, **40**, 442 (1948).

Summary

The physical meaning of four empirical correlation rules of azeotropic data, i.e. two types of Lecat's, Denyer et al.'s and Skolnik's rules, is clarified simultaneously with their mutual relations, by using the equations derived in part I and the assumption of constancy of molecular interchange energy for homologous azeotropes found in part II of the series of this study. The theoretically derived equations by Kuhn et al. are also given as a limiting case of ours.

The author wishes to express his hearty thanks to Mr. Yo-ichiro Mashiko for his kind guidance and encouragement throughout this work.

Government Chemical Industrial Research Institute, Yoyogi, Tokyo

Estrogenic Biphenyls. I. 2,3'-Diethyl-4-methoxybiphenyl-4'-carboxylic Acid

By Michinori ŌKI* and Takeo SATO

(Received February 11, 1957)

In connection with the hypothesis, proposed by one of the present authors (M.O.) and Y. Urushibara[1], which postulates that the estrogenic compounds should possess not only two active hydrogens at the optimum distance apart, but the optimum thickness or width of the molecule, a number of stilbene derivatives were synthesized and found to be estrogenic[2-4]. A compound is supposed to be estrogenic from the standpoint of this hypothesis if

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1) M. Ōki and Y. Urushibara, This Bulletin, **25**, 109 (1952).

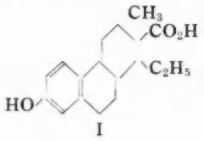
2) M. Ōki, ibid., 112.

3) idem, ibid., **26**, 66 (1953).

4) idem, ibid., 331.

it carries two active hydrogens at the optimum distance regardless of their nature.

Thus, doisynolic acid (I) and bisdehydrodoisynolic acid (II) are powerful estrogens[5] in spite of the facts that their



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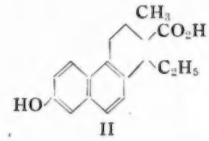

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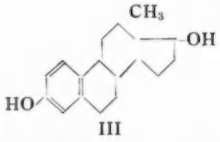
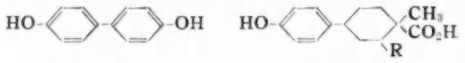


III

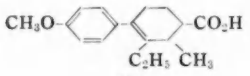
structures are different from that of the natural estrogen, estradiol (III), and that two active hydrogens are born by a hydroxyl and a carboxyl group.

Dodds et al.[6] reported that 4,4'-dihydroxybiphenyl (IV) was almost inactive. The fact seems probable, since this molecule is planar and the distance between two active hydrogens is less than the optimum. The authors postulate that even a biphenyl derivative can be a potent estrogen if it carries two active hydrogens at the optimum distance and possesses the optimum thickness of the molecule.

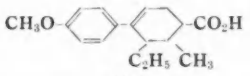
Novello et al.[7] prepared 2-alkyl-4-(*p*-hydroxyphenyl)-1-methylcyclohexanecarboxylic acids (V) and reported that they were estrogenic. Although these types of compounds are not the biphenyl derivatives, the result encouraged the authors to investigate the biphenyl series. Furthermore, while this paper was in preparation Nathan and Hogg[8] reported that 2-methyl-3-ethyl-4-(*p*-anisyl)-3-cyclohexenecarboxylic acid (VI) and its 4-unsaturated isomer (VII) were highly estrogenic.



IV V

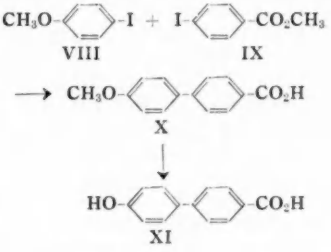


VI

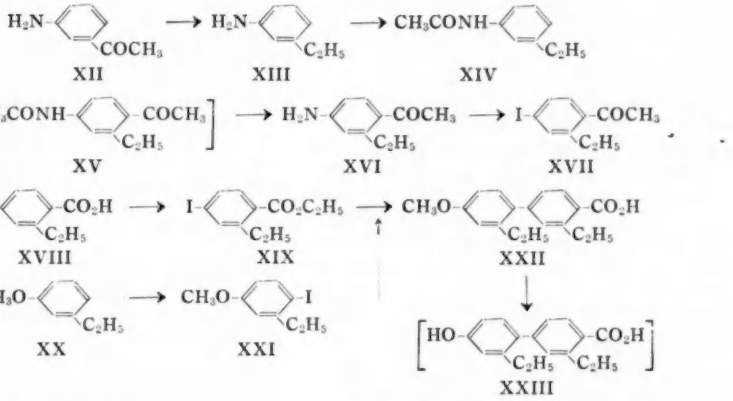


VII

4-Hydroxybiphenyl-4'-carboxylic acid (XI) possesses, from the measurement of its scale model, two active hydrogen atoms at the suitable distance and, therefore, was supposed to be an estrogen, although the activity might be slight due to its planar structure. This substance was synthesized by the method described below and, as expected, showed estrogenic activity to 60% of the tested animals (ovariectomized mice) at the dose of 500γ.



VIII IX X XI



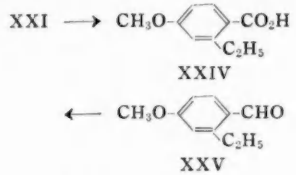
XII XIII XIV XV XVI XVII XVIII XIX XX XXI XXII XXIII

5) K. Miescher, *Chem. Rev.*, **43**, 367 (1948).
6) E. C. Dodds and W. Lawson, *Proc. Roy. Soc. (London)*, **B125**, 222 (1938).
7) F. C. Novello, M. E. Christy and J. M. Sprague, *J. Am. Chem. Soc.*, **76**, 738 (1954).
8) A. H. Nathan and J. A. Hogg, ibid., **78**, 6163 (1956).

In order to give thickness and width to this molecule, the introduction of alkyl groups was attempted. Two benzene rings in biphenyl derivatives, as well known[9], cannot take coplanar structure when a substitution takes place at 2- or 2'-position. Thus thickness will be given to the molecule. As an example, 4-methoxy-2,3'-diethylbiphenyl-4'-carboxylic acid (XXII) was prepared. An ethyl group at 2-position was introduced to give steric hindrance by its bulk and to rotate benzene rings out of the coplanar structure. Another ethyl group at 3'-position was to give the optimum width of the molecule by analogy of the ethyl group next to the carboxyl group in doisynolic acid, in which, when the ethyl group is replaced by a methyl group or hydrogen, only weaker estrogenic activity is produced.

The synthesis of compound XXII is illustrated in the chart of page 509. *m*-Aminoacetophenone (XII) was reduced by modified Wolff-Kischner method[10] to *m*-ethylaniline (XIII) and the latter was acetylated. *m*-Ethylacetanilide (XIV) was treated with acetyl chloride and aluminum chloride and the product (XV) was hydrolyzed to give 2-ethyl-4-aminoacetophenone (XVI). The aminoketone (XVI) was converted into the iodo compound (XVII) through diazo reaction and the iodoketone was oxidized by sodium hypobromite to 2-ethyl-4-iodobenzoic acid (XVIII), which was esterified in the usual way. 3-Ethyl-4-iodoanisole (XXI) was prepared by direct iodination of *m*-ethylanisole (XX) in the presence of yellow mercuric oxide and submitted to the Ullmann reaction with ester XIX. Attempted demethylation of 2,3'-diethyl-4-methoxybiphenyl-4'-carboxylic acid (XXII) to 2,3'-diethyl-4-hydroxybiphenyl-4'-carboxylic acid (XXIII) with hydrogen bromide was unsuccessful.

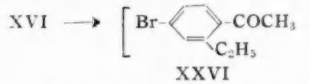
The structural proof of 3-ethyl-4-iodoanisole was obtained in the following way. On treatment with magnesium and then with solid carbon dioxide, compound XXI yielded a carboxylic acid (XXIV). On the other hand, 2-ethyl-4-methoxybenzaldehyde (XXV)[11], prepared through modified Gattermann reaction, was oxidized by potassium permanganate to yield a carboxylic acid melting at 122–123°. These two acids were found to be identical by the mixed melting point determination.



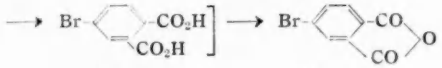
XXIV

XXV

The structure of 4-amino-2-ethylacetophenone (XVI) was proven as illustrated in the following diagram. The amino group of XVI was replaced by bromine and 4-bromo-2-ethylacetophenone (XXVI) was oxidized with nitric acid and then with potassium permanganate. The dibasic acid (XXVII) was sublimed in vacuo and a produced anhydride did not depress the melting point on admixture with the authentic sample of 4-bromophthalic anhydride (XXVIII)[12].

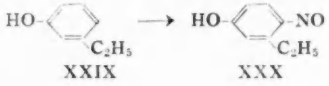


XXVI

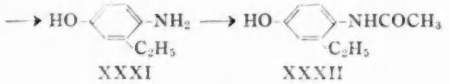


XXVII XXVIII

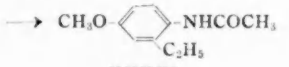
3-Ethyl-4-iodoanisole (XXI) might be synthesized through diazo reaction of 2-ethyl-4-anisidine. *m*-Ethylphenol (XXIX) was nitrosated and the product was reduced to the corresponding aminophenol (XXXI). The amino group was protected by acetylation and the hydroxyl group was methylated with dimethyl sulfate. But, before completion of this series, a more successful method than this rather lengthy one was found as described above. Therefore this method was discarded.



XXIX XXX



XXXI XXXII



XXXIII

The active dose was determined by the vaginal smear test with ovariectomized

9) R. A. Riedel, M. Orchin and L. Reggel, ibid., **70**, 199 (1948); E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

10) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946); **70**, 2802 (1948); **71**, 3301 (1949).

11) B. R. Baker, ibid., **65**, 1572 (1943).

12) K. Fries and E. Hübner, *Ber.*, **39**, 435 (1906).

mice. The substance XXII was dissolved in oil and subcutaneously injected. The minimum active dose to produce estrus in 100% was found to be 100 γ.

Experimental*

***m*-Ethylaniline (XIII).**—A solution of 135 g. (1 mole) of *m*-aminoacetophenone (XII) prepared by reduction[13] of *m*-nitroacetophenone, 280 g. of potassium hydroxide and 120 g. (2 moles) of hydrazine hydrate in 700 ml. of diethylene glycol was heated to reflux for one hour. After this period the reflux condenser was removed and the low-boiling materials were collected with a downward condenser until the reaction mixture attained the temperature of 200°. The reaction mixture was refluxed for further three hours and steam-distilled. The distillate was combined with the one obtained before heating at 200° and extracted with ether. The combined extracts were dried over potassium carbonate and distilled under reduced pressure, b.p. 75–76°/4 mm. Yield 80–90%. The melting point of the acetyl derivative was 24° (reported[14] melting point is 24°). *m*-Ethylphenol was prepared[14] through diazo reaction of this compound.

3-Ethyl-4-nitrosophenol (XXX).—To a well stirred solution of 43 g. (0.34 mole) of *m*-ethylphenol (XXIX) in 200 ml. of 95% alcohol and 200 ml. of concentrated hydrochloric acid, was added 35 g. (0.5 mole) of sodium nitrite in small portions, while the temperature was maintained at 0–2°. After the addition was finished, stirring was continued for ten minutes and the mixture was poured into 2 l. of water. Crystals were collected and recrystallized from benzene. Colorless needles, m.p. 135° (decomp.). Yield, 40 g. or 74% of the theoretical.

Anal. Found: N, 9.52. Calcd. for $C_8H_9O_2N$: N, 9.27%.

4-Amino-3-ethylphenol (XXXI).—To a solution of 20 g. (0.13 mole) of the compound XXX in 200 ml. of concentrated aqueous ammonia and 300 ml. of water, was introduced hydrogen sulfide. Crystals began to separate from the solution after five to ten minutes and the color of the solution changed. Hydrogen sulfide was passed through the solution for further forty-five minutes and the crystals were collected.

It was the most convenient way to use this crude material for the next reaction, since this compound was unstable and did not keep well. The analytical sample was obtaind in colorless plates by recrystallization from water, m.p. 169.5–171° (decomp.). Yield 15.5 g. or 85% of the theoretical.

Anal. Found: N, 10.33. Calcd. for $C_8H_{11}ON$: N, 10.20%.

4-Acetamido-3-ethylphenol (XXXII).—Fifteen grams (0.11 mole) of the crude aminophenol (XXXI) was treated with 25 g. of acetic anhydride. On recrystallization from water, were obtained colorless plates which melted at 137.5–139°. This compound took a molecule of water of crystallization, as analysis indicated, solidified over the first melting point and remelted at 173°. Yield 17 g. or 77% of the theoreticlal.

Anal. Found: N, 7.25. Calcd. for $C_{10}H_{13}O_2N \cdot H_2O$: N, 7.07%.

4-Acetamido-3-ethylanisole (XXXIII).—To a solution of 40 g. (0.2 mole) of the compound XXXII in 10 g. (0.25 mole) of sodium hydroxide and 200 ml. of water, was dropwise added 30 g. (0.24 mole) of dimethyl sulfate at 30–40°, while the mixture was well stirred. The crystals were collected and recrystallized from aqueous alcohol (1 : 1). Colorless needles, m.p. 118–119°. Yield 35 g. or 89% of the theoretical.

Anal. Found: N, 7.28. Calcd. for $C_{11}H_{16}O_2N$: N, 7.21%.

4-Methoxybiphenyl-4'-carboxylic Acid (X).—Methyl *p*-iodobenzoate (IX) was prepared[15] from *p*-iodobenzoic acid and methanol and *p*-iodoanisole (VIII)[16] from anisole and iodine. A mixture of 2.5 g. (0.0095 mole) of the compound IX and 5.5 g. (0.0235 mole) of VIII was preheated at 230° and 8.0 g. (0.125 atom) of copper bronze activated by Kleiderer and Adams' method[17] was added in portions with good stirring, while the temperature was maintained at 230–240°. The addition required twenty minutes. Then the temperature was raised to 280° and the reaction mixture was stirred for forty minutes at that temperature. After cooling, the mixture was extracted with acetone, the solvent was evaporated and the residue was refluxed with 10% sodium hydroxide solution in aqueous alcohol (1 : 1) for two hours. After dilution with 500 ml. of water active charcoal was added and filtered off to remove adherent oil. The filtrate was acidified with hydrochloric acid. The crystals were collected, boiled with 30 ml. of acetic acid and the mixture was filtered to remove insoluble material. The filtrate was concentrated and gave, on cooling, crystals melting at 247°. The compound gave no depression in the mixed melting point with the authentic 4-methoxybiphenyl-4'-carboxylic acid[18] prepared by oxidation of the corresponding acetyl compound. The reported melting point is 248–249°[18,19].

4-Hydroxybiphenyl-4'-carboxylic Acid (XI).—The compound X was demethylated according to the method of Fieser and Bradsher[18]. m.p. 259°.

3-Ethyl-4-iodoanisole (XXI).—To a solution of 44 g. (0.33 mole) of *m*-ethylanisole (XX),

* All boiling and melting points are uncorrected.

13) K. Buchka, *Ber.*, **10**, 1714 (1877); C. Engler, ibid., **11**, 930 (1878); L. C. King, M. McWhirter and D. M. Barton, *Ann.*, **67**, 2091 (1945).

14) Mm, A. Behal and E. Choay, *Bull. soc. chim. France*, (3), **11**, 206 (1894).

15) H. Schmidt and G. Schultz, *Ann.*, **207**, 320 (1881)

16) M. P. Brenans, *Bull. Soc. chim. France*, (3), **25**, 819 (1901).

17) E. C Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4225 (1933).

18) L. F. Fieser and C. K. Bradsher, ibid., **58**, 1738 (1936).

19) W. S. Johnson, C. D. Gutsche and R. O. Offenhauer, ibid., **68**, 1648 (1946).

prepared by methylation[20] of *m*-ethylphenol, in 70 ml. of alcohol were alternatively added 86 g. (0.4 mole) of yellow mercuric oxide and 84 g. (0.33 mole) of iodine in small portions with good swirling, while the temperature was maintained below 30°. The reaction mixture was finally heated on a water bath for ten minutes and filtered after cooling. Water was added to the filtrate and oil was extracted with ether. The combined extracts were sucessively washed with water, aqueous potassium iodide, and again with water, and dried over calcium chloride. After evaporation of the solvent, the residue was fractionated under diminished pressure. The main portion boiled at 147–150°/18 mm. and the pure compnund was obtained on redistillation, b. p. 120–120.5°/5 mm. Yield 60 g. or 76% of the theoretical.

Anal. Found: I, 48.63. Calcd. for $C_9H_{11}OI$: I, 48.39%.

2-Ethyl-4-methoxybenzoic Acid (XXIV). (A) From 3-Ethyl-4-iodoanisole (XXI).—A mixture of 5 g. (0.019 mole) of 3-ethyl-4-iodoanisole (XXI), 0.7 g. (0.029 atom) of magnesium and 50 ml. of ether was heated under reflux for one hour. To the Grignard reagent, a piece of solid carbon dioxide was added and, when the mixture attained room temperature, hydrochloric acid was added to decompose the complex. The aqueous layer was extracted with ether and the combined extracts were concentrated. The ethereal layer was extracted with 50 ml. of 10% aqueous sodium hydroxide; the aqueous layer was treated with active charcoal and acidified with hydrochloric acid. The crystals were collected and recrystallized from aqueous alcohol. Colorless plates, m.p. 120–121°. Yield 1.5 g. or 43% of the theoretical.

(B) From 2-Ethyl-4-methoxybenzaldehyde (XXV).—A suspension of 2-ethyl-4-methoxybenzaldehyde (XXV)[11] in excess aqueous potassium permanganate was heated on a water bath for thirty minutes. Sulfur dioxide was introduced to the suspension and crystals were collected. On recrystallization of the alkali soluble part from aqueous alcohol, there were obtained colorless plates melting at 122–123°.

Anal. Found: C, 66.32; H, 6.82. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%.

The melting point did not depress when both samples were mixed.

4-Amino-2-ethylacetophenone (XVI).—To a well stirred solution of 41 g. (0.25 mole) of *m*-ethylacetanilide (XIV) and 35 g. (0.45 mole) of acetyl chloride in 200 ml. of carbon disulfide, was added 116 g. (0.87 mole) of powdered aluminum chloride in portions of ca. 20 g. After the addition, the reaction mixture was heated under reflux for one hour and left to stand at room temperature for two hours. The supernatant carbon disulfide layer was decanted and the lower layer was decomposed with ice and hydrochloric acid. The aqueous layer was decanted off and the lower layer was hydrolyzed by heating with 200 ml. of dilute hydrochloric acid (1 : 1) for two hours. The cooled hydrolysate was basified with sodium hydroxide and the organic base was extracted with ether. The ethereal extracts were dried over potassium carbonate and fractionated. A fraction which boiled at 150–162°/5 mm. gave a pure sample on refractionation (b.p. 159–161°/5 mm.). The distillate solidified on cooling and the solid was recrystallized from benzene-petroleum ether. Colorless needles, m.p. 62–63°. Yield 16.5 g. or 40% of the theoretical.

Anal. Found: N, 8.66. Calcd. for $C_{10}H_{13}ON$: N, 8.58%.

4-Bromophthalic Anhydride (XXVIII).—To a diazonium solution obtained from 7.0 g. (0.043 mole) of 4-amino-2-ethylacetophenone (XVI), 20 ml. of 48% hydrobromic acid and 3.5 g. (0.051 mole) of sodium nitrite, was added a small amount of copper bronze. The mixture was heated on a water bath to complete the reaction and extracted with ether. The extracts were washed with aqueous sodium hydroxide and ether was evaporated. The residue was refluxed with dilute nitric acid, which was composed of 10 ml. of nitric acid (d; 1.38) and 40 ml. of water, for five hours. After cooling, the crystalline material was collected and further oxidized by aqueous potassium permanganate. A dicarboxylic acid, thus obtained, was sublimed under reduced pressure. Colorless plates, m.p. 105–106°. The compound did not depress the melting point on admixture with the authentic specimen of 4-bromopthalic anhydride (XXVIII) prepared through oxidation[21] of 1,6-dibromo-2-naphthol followed by sublimation[12].

2-Ethyl-4-iodoacetophenone (XVII).—A solution of 3-ethyl-4-acetylbenzenediazonium sulfate prepared from 33 g. (0.2 mole) of the compound XVI, 42 g. (0.4 mole) of concentrated sulfuric acid, 100 ml. of water and 14 g. (0.2 mole) of sodium nitrite in 30 ml. of water, was added to a hot solution of 50 g. (0.3 mole) of potassium iodide in 200 ml. of water. The organic material was extracted with ether and the ethereal extracts were successively washed with aqueous sodium hydroxide, aqueous sodium thiosulfate and water. After drying over calcium chloride, the solvent was evaporated and the residue was distilled under reduced pressure. Colorless oil, b.p. 166°/20 mm. Yield 33 g. or 60% of the theoretical.

Anal. Found: I, 46.30. Calcd. for $C_{10}H_{11}OI$: I, 46.80%.

2,4-Dinitrophenylhydrazone of XVII was prepared in the usual way. Scarlet needles, m.p. 152–153°.

Anal. Found: N, 12.61. Calcd. for $C_{16}H_{15}O_4N_4I$: 12.34.

2-Ethyl-4-iodobenzoic Acid (XVIII).—To a sodium hypobromite solution prepared from 79.9 g. (0.5 mole) of bromine, 63 g. (1.6 moles) of sodium hydroxide and 400 ml. of water, was dropwise added a solution of the compound XVII in 170 ml. of dioxan over a period of one hour, during which time stirring was applied and the

20) c. f. G. S. Hiers and F. D. Hager, "*Org. Synth.*," Coll. Vol. **1**, (1940), p. 58.

21) c. f. A. F. Smith, *J. Chem. Soc.*, **35**, 789 (1879).

temperature was maintained below 20°. The reaction was completed by heating on a water bath for 10 minutes and the excess of hypobromite was decomposed with sodium bisulfite. Bromoform was removed by steam distillation and the remainder was acidified with hydrochloric acid. The solid was collected and recrystallized from aqueous alcohol. Colorless needles, m.p. 130–131°. Yield 25 g. or 83% of the theoretical.

Anal. Found: I, 46.23. Calcd. for $C_9H_9O_2I$: I, 45.99%.

Ethyl 2-Ethyl-4-iodobenzoate (XIX).—A solution of 5.0 g. of the acid (XVIII) and 5 ml. of concentrated sulfuric acid in 25 ml. of ethanol was heated under reflux for four hours. After cooling, the mixture was diluted with 100 ml. of cold water and extracted with ether. The ester boiled at 166–168°/17 mm. Yield 5.0 g. or 90% of the theoretical.

Anal. Found: I, 42.03. Calcd. for $C_{11}H_{13}O_2I$: I, 41.76%.

2,3'-Diethyl-4-methoxybiphenyl-4'-carboxylic Acid (XXII).—The Ullmann reaction was carried out in the same way as described in the preparation of X, using 5.0 g. (0.016 mole) of the compound XIX, 10 g. (0.038 mole) of XXI and 10.0 g. (0.157 atom) of activated copper bronze. The acidic portion was dissolved in ether and passed through an alumina column. On recrystallization from aqueous alcohol of the compound from the eluent, colorless prisms melting at 136.5–137° were obtained. Yield 0.5 g. or 10% of the theoretical based on the amount of the compound XIX.

Anal. Found: C, 76.34; H, 7.21. Calcd. for $C_{15}H_{20}O_3$: C, 76.03; H, 7.09%.

The authors wish to express their hearty thanks to Professor Y. Urushibara, the University of Tokyo, for his kind guidance and encouragement and to the Research Department of Teikoku Hormone Manufacturing Co., Ltd., Kawasaki, for bioassays. The authors' thanks are also due to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

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Dielectric Investigation on Coals. I. Dielectric Properties of Japanese Coals

By Isao MIYASITA and Keniti HIGASI

(Received January 22, 1957)

Introduction

Little information exists in the literature of the subject concerning the dielectric constant of coals. In 1948 Bond, Griffith and Maggs[1] reported a dielectric study of coals containing absorbed water. Their emphasis was then placed on the freezing mechanism of the water below 0°C and no reliable measurement was made on the dielectric constant of coal itself*.

In 1955 van Krevelen and his co-workers[2] published a report on dielectric constants of low rank and bituminous coals. The coal samples treated in their study were reduced to fine powders and the dielectric constant of the powders was indirectly estimated by the use of an immersion method. As is known with certainty, the conditions of their measurement were not free from errors of various sources. For instance, no reliable data are to be obtained in the region of the anomalous dispersion which is expected to occur from the dielectric heterogeneity of the measured system[3]. They measured apparent dielectric constants of binary mixtures composed of coal powder and an immersion liquid such as diisopropyl ether. In order to secure accuracy of measured values it is desirable that the measurements be made covering a wide range of frequencies or of temperatures. But actually their measurements were limited to a single frequency of 1 Mc/s at room temperature.

Since 1953 a dielectric investigation[4,5]

1) R. L. Bond, M. Griffith and F. A. P. Maggs, *Disc. Faraday Soc.*, **3**, 29 (1948).

2) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

* There are available other papers in which the dielectric method was employed to estimate the moisture content in coals. See, for example, W. Klempt, *Brennstoff-Chem.*, **34**, 294 (1953); H. Oikawa, *J. Coal Res. Inst.*, (Tokyo), **3**, 137 (1952).

3) K. W. Wagner, *Arch. Elektrotech.*, **2**, 371 (1941); R. W. Sillars, *J. Inst. Elec. Engrs.*, **80**, 378 (1937).

4) I. Miyasita, *Bull. Res. Inst. Appl. Elec.*, Hokkaido Univ., **5**, 123, (1953), **6**, 117 (1954).

5) I. Miyasita, R. Miura and K. Higasi, This Bulletin **28**, 148 (1955).

TABLE I

CHEMICAL ANALYSIS OF COALS USED FOR DIELECTRIC STUDIES*

(Composition on moisture-free basis, wt. %)

Coal No.	Seam	Ash	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
I	Moziri, No. 4	5.12	85.25	5.89	6.91	1.72	0.23
II	Moziri, No. 3	11.85	81.71	5.93	9.78	2.00	0.58
III	Moziri, No. 9	3.55	82.98	5.92	9.07	1.89	0.14
IIIa	Moziri, No. 11	8.83	82.07	5.92	9.86	1.81	0.34
IV	Akabira, No. 11	6.80	80.76	5.91	—	—	—
V	Mitui-Bibai, No. 3-4	2.94	80.47	5.87	—	—	—
Va	Mitui-Bibai, No. 4-4	3.87	80.12	5.78	—	—	—
Vb	Mitui-Bibai, No. 1-5	4.12	78.40	5.78	—	—	—
Vc	Mitui-Bibai, No. 1-3	5.00	80.62	5.71	11.55	1.88	0.24
VI	Tempoku (brown coal)	1.22	66.62	5.26	—	—	—

* The writers' thanks are due to Mr. Y. Zyomoto for providing the data of this Table.

on coals has been under way in the laboratory of the present writers. In the present article of this series detailed description will be presented of the results obtained for ten coal samples from Hokkaido mines, Japan. It may be worth while to point out that successful dielectric determination was done on coals themselves for the first time. Further, a wide range of frequencies between 50Mc/s and 300 c/s was used in the present measurement.

Material and Method

Samples were prepared from the following ten coals (See Table I). For the sake of convenience, they have been arranged in order according to the geological age of the coal bed concerned. Coals (I)—(Vc): Hokkaido bituminous coals. Coal (VI): Tempoku brown coal, Hokkaido mine. Analyses of the coal samples are given in Table I.

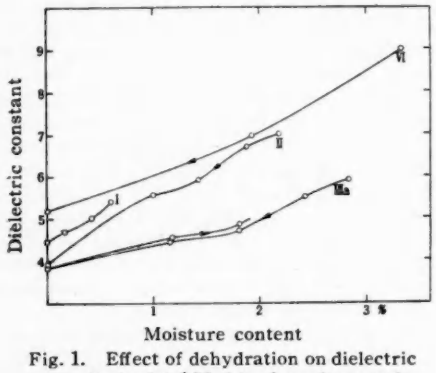

Fig. 1. Effect of dehydration on dielectric constants (at 1 Mc/s) of various coals. I, II, IIIa: Moziri bituminous coal; VI: Tempoku brown coal (cf. Table I). There is uncertainty as to the state of absolute drying.

Coal blocks which were rich in vitrain but had no cracks, were selected, carefully cut, ground, polished and finally made into the form of a circular plate of 5 ± 0.1 mm. thick and 40 mm. in diameter. No sort of binding material such as Canada balsam was employed in the preparation of the disks.

The disks thus prepared were dried in a desiccator over phosphoric anhydride for three or four months. The presence of moisture in the sample usually results in obtaining a higher dielectric constant than expected (see Fig. 1). It is often accompanied by an anomalously large loss factor in the lower frequency region. Therefore, the complete removal of moisture was concluded to have been accomplished when the dielectric constant (especially measured in the lower frequency side) was low and became unchanged by further desiccation. Further check on this process of drying was made for one sample coal (IIIa) by making a comparison with another method of drying. The same material dried at 105°C in air for 28 hours gave little difference in dielectric constant.

The dielectric measurements were made with a Q-meter (Yokogawa QM-101) for the frequency range of 50 Mc/s to 50kc/s, and with an impedance bridge (Yokogawa BV-z-103A) for the range of 20kc/s to 300c/s. To attain a higher accuracy of the impedance bridge in the measurement of low-loss materials, a special device was necessary*. For this purpose, a combined unit of a narrow-band amplifier and a cathode-ray oscillograph was employed to detect the balance in the bridge circuit. Further, the source for the Q-meter was regulated with an automatic stabilizer.

Aluminium foils of 38 mm. diameter were pasted on the surfaces of the coal disk. They were connected with electrodes of the same 38 mm. diameter. The same electrodes were used both with the Q-meter and with the impedance bridge.

Readings of the Q-meter were taken when a resonance was established. After the test piece was removed resonace was regained by the use

* Detailed description of this device will be reported elsewhere (I. Miyasita, to be published in *Bull. Inst. Appl. Elec.*, Hokkaido University).

TABLE II

VARIATION OF DIELECTRIC CONSTANT (ε') AND LOSS FACTOR (ε'') WITH FREQUENCY AT ROOM TEMPERATURE

Coal	No.	300 c	1 kc	3 kc	10 kc	20 kc	100 kc	300 kc	1 Mc	10 Mc	50 Mc
I	ε'	4.56	4.55(4.54)	4.54	4.52	4.37	4.49	4.52	4.47	4.41	4.49
	ε''	—	0.0395	—	—	—	0.0346	0.0347	0.0351	0.0325	0.0318
II	ε'	4.51	4.37(4.37)	4.28	4.15	4.08	4.15	3.96	3.92	3.82	3.80
	ε''	—	0.0926	—	—	—	0.080	0.076	0.075	0.070	0.058
III	ε'	4.01	3.99(3.94)	3.97	3.96	3.86	3.92	3.88	3.88	3.86	3.83
	ε''	—	0.0334	—	—	—	0.0204	0.0173	0.0173	0.0189	0.021
IIIa(1)	ε'	4.25	4.19	4.14	4.12	4.05	3.99	3.90	3.85	3.78	3.74
	ε''	—	—	—	—	—	0.0585	0.0447	0.0424	0.0308	0.0278
IIIa(2)	ε'	4.07	3.98(3.85)	3.93	3.88	3.81	3.70	3.69	3.69	3.69	3.70
	ε''	—	0.0404	—	—	—	0.032	0.0216	0.0238	0.0181	0.0228
IV	ε'	3.76	3.75	3.75	3.66	3.66	3.66	3.61	3.66	3.61	3.46
	ε''	—	0.0325	—	—	—	0.0206	0.0169	0.0166	0.0169	0.0204
V	ε'	3.76	3.74	3.74	3.71	3.59	3.64	3.69	3.61	3.64	3.69
	ε''	—	0.0224	—	—	—	0.0128	0.0109	0.0124	0.012	0.014
Va	ε'	4.42	4.34(4.30)	4.30	4.20	4.11	4.12	4.10	4.10	4.08	4.14
	ε''	—	(0.0316)	—	—	—	—	—	—	—	—
Vb	ε'	4.5	4.42(4.25)	4.28	4.28	4.16	4.23	4.23	4.19	4.16	4.16
	ε''	—	(0.0442)	—	—	—	0.030	0.0266	0.0288	0.0268	0.0337
Vc	ε'	4.73	4.70	4.57	4.48	4.38	—	—	—	—	—
VI	ε'	5.65	5.56	5.5	5.4	5.28	5.35	5.35	5.20	5.10	5.25
	ε''	—	—	—	—	—	0.0815	0.0768	0.0856	0.101	0.137

of an auxiliary condenser when the two electrodes came to be the same distance apart. Dielectric constant and loss factor of the sample were obtained by simple calculations from the readings at the resonance points. Procedure with the impedance bridge was essentially the same as those described in the usual text book.

The range of errors in the measured quantities is largely dependent upon the frequency of the measurement. Broadly speaking the Q-meter and the impedance bridge, after the improvement above noted are believed to give errors of less than $\pm 2\%$ in dielectric constant, while the loss factors are more sensitive in respect to conditions of the measurement.

As none of the test pieces prepared from coal samples was a perfectly circular disk with two perfectly flat surfaces, error arising from the irregularity of the shape demanded special attention. Regarding edge effects, Prof. Miura of the electrical engineering dept. of this University kindly took the trouble to examine the error involved. Further, two sorts of calibration experiments were conducted: first, with a test piece of variable edge; second, comparison with Hartshorn's[6] procedure regarding this correction. Error of the edge irregularity in the dielectric constant was inferred thus to be only a small percent, or less than 5%.

Concerning the unflat surfaces, the use of aluminium foil was believed to help diminish the principal error, which arises from the possible air gap between the electrodes and the test piece. Both the inhomogeneity of the sample and the existence of ash and moisture provided other difficulties, of which the latter is more important. Every effort was made to eliminate errors arising from all these effects, but they were not always estimable. Probably one may assume that the maximum error in the absolute value in dielectric constant amounts to about 5% or near to it. Loss factors in general are more liable to errors than dielectric constants, but they are less significant in the interpretation of the results.

Measurements were carried out at room temperature. For some samples, (IIIa) (Va) and (V), measurements were also made at 100°C, but no appreciable difference was found in the dielectric constant values.

Experimental Results

Results of the measurement are collected in Table II. Values in parentheses are those redetermined after the lapse of a few months (in a desiccator). In sample (IIIa) two test pieces prepared from the same coal specimen were examined (Compare IIIa(1) and IIIa (2) in Table II). One gave a higher value in dielectric constant than the other by the amount 0.04—0.29. The choice of the two pieces was not made at random—they were selected from blocks of entirely different appearance but the same specimen. Therefore this deviation of less than $\pm 10\%$ may suggest the range of maximum deviation in the dielectric constant which arises from any individual difference of the sample.

Perhaps the most remarkable feature in this table is that, over a wide range of frequency, observed dielectric constants show values of less than 5, while loss factors have small values below 0.1. Only one exception is found in the brown coal (VI).

There are available no refractivity data for Japanese coals. But according to our microwave measurement on Mayazi coal (83.14% carbon), its high frequency dielectric constant was 3.37[7].

6) L. Hartshorn and W. H. Ward, *Proc. Inst. Elec. Engrs.*, **79**, 597 (1936).

7) K. Higasi, I. Miyasita and Y. Ozawa, this Bulletin, **30**, 546 (1975).

Further it is reported that the refractive index for European coals amounts to 1.7-2.0[8]. Therefore it may be reasonable to suppose that the observed dielectric constants should be only slightly larger than the square of the corresponding refractive index, the difference being less than 2[5]. These points will be discussed fully in subsequent papers.

Discussion

To begin with, the dielectric constants measured at two frequencies, 1 kc/s and 1 Mc/s, are plotted against the carbon content (dry, ash-free) of the coal. For the sake of comparison the dielectric constants at 1 Mc/s given by van Krevelen[2] are plotted in the same figure. Full discussion on this problem will be given when ample data on a variety of coals are provided from the investigation on coal powders.

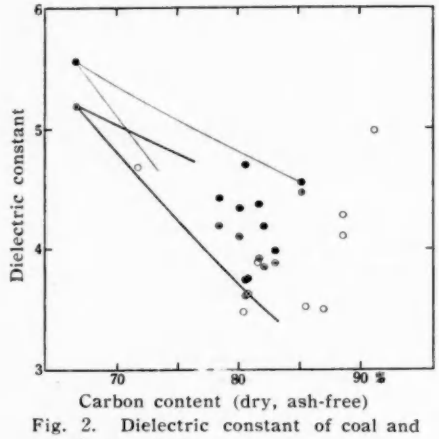

Fig. 2. Dielectric constant of coal and carbon content.
● 1 Mc } Present research
● 1 kc }
○ 1 Mc Krevelen's data for strongly dried coal.

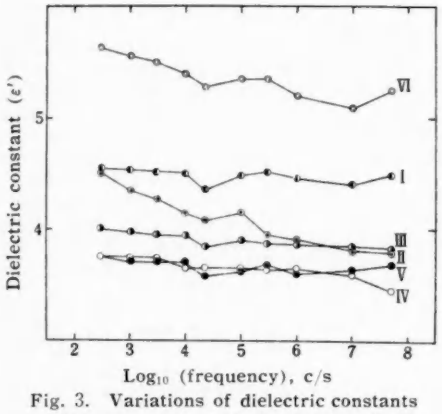

Fig. 3. Variations of dielectric constants of various coals with frequency. I, II, III: Moziri coal; IV: Akabira coal; V: Mituibibai coal; VI: Tempoku coal (cf. Table I).

In the present article attention will be focussed on the frequency dependence of dielectric constants and loss factors. These quantities, when directly obtained from coals themselves, are free from errors due to dielectric inhomogeneity. At a glance at the ε' curves in Fig. 3, one is impressed by the fact that the curves for (I), (III), (IV), (V) are nearly flat and run almost parallel. That is, they are non-dispersive in the whole range of the measured frequencies 300 c/s - 50 Mc/s. Slight increases at the lower frequency side are found in the curves of (II) and (VI), but they are not very pronounced.

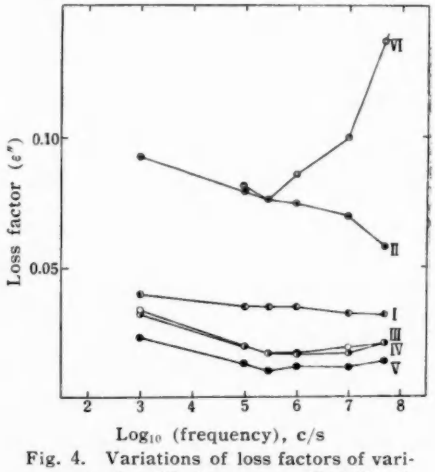

Fig. 4. Variations of loss factors of various coals with frequency. Coal No. I, II, III, etc: ditto (cf. Table I).

The curves for loss factors (Fig. 4) are of interest in this connection. It will be confirmed from loss factor that there is no anomalous dispersion in the samples of (I), (III), (IV) and (V). Samples (II) and (VI) have larger loss factors than others, but the frequency dependence is entirely different between the two. The loss factor ε'' of (II) gradually decreases at the higher frequency side, while that of (VI) sharply increases. This may suggest that the mechanism of dielectric absorption is different in the above two cases. From among the data not reproduced in Figs. 3 and 4, the samples of (IIIa2) and

8) D. W. van Krevelen, *Brennstoff-Chem.*, **34**, 167 (1953).

(Vb) are to be classified in the same group as (II) from the frequency dependence of the loss factor.

There are two types of causes which produce dielectric dispersion. One is the existence of movable dipoles in the system. In certain polymers and organic crystals dipoles are not completely blocked from rotation, producing distinct dispersion phenomena[9]. In Fig. 5, dielectric behavior of phenol-formaldehyde resin[10] is compared with that of Tempoku brown coal. It is generally accepted that the dielectric losses of this plastic are mainly determined by the rotation of the polar

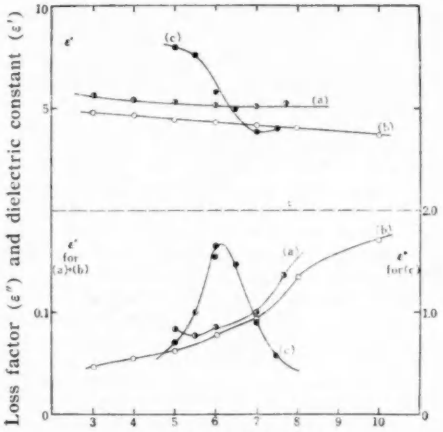

Fig. 5. Two types of dielectric dispersion.
(a) Tempoku brown coal.
(b) Phenol-formaldehyde resin.
(c) A mixture of coke-paraffin wax.

OH groups of the structure. Similarly Tempoku coal may have some polar groups such as OH group which have freedom of rotation to a certain extent. However, there is not any of the coals which exhibits dispersive charactor so clearly as Tempoku coal (Figs. 3 and 4). Most of the bituminous coals behave like non-polar substances. It seems reasonable to suppose, therefore, that in these coals the polar groups are in a state of non-rotation with the electric field applied from outside.

The other important cause of dielectric dispersion is the dielectric heterogeneity of the system. For the sake of illustration, the dielectric properties of a mixture of coke-paraffin wax[11] are shown in curves (c) in Fig. 5. A peak in the loss factor is observed at a particular frequency when a semi-conductive particle of coke is surrounded by paraffin medium with good insulating power. Indeed, the direct current conductivity of coke itself is calculable with some precision from that frequency by the use of Wagner-Sillar's theory[3,11].

It is of some interest in this connection that Ellis[12] advanced a proposition that there exist units of graphite structure in bituminous coals. If such structure corresponds to particles of semi-conductive nature, the situation may not be essentially different from that of a coke-paraffin wax system. As far as the coals treated in the present experiment are concerned, no such dispersion phenomenon was observed as would support Ellis's view on the graphite micellar structure*.

Lastly, let attention be directed to the increase of loss factor at the lower frequency region as observed in curve II in Fig. 4. There are two reasons for believing that this increase is due to the trace of water in the system. First, this sort of increase in loss factor becomes very pronounced in all the materials which are not completely dried. Second, the phenomenon itself can be theoretically accounted for by Sillar's calculation[3] on the assumption that in cracks of the coal there is some trace of water particles of elongated shape.

Summary

In a wide frequency range covering 300 c/s to 50 Mc/s dielectric constant and loss factor of ten Japanese coals were measured at room temperature. The result provides a view that Japanese coals are almost non-polar in effect and embrace no units of graphite structure of the sort proposed by Ellis.

The writers wish to thank Prof. G. Takeya and Assit. Profs. R. Miura and M. Kugo for friendly help and stimulating discussions.

Research Institute of Applied Electricity
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9) C. P. Smyth, "Dielectric Behavior and Structure," Chap. V, McGraw-Hill Book Co. (1955).
10) L. Hartshorn L. V. L. Parry and E. Rushton, *Proc. Inst. Elec. Engrs.*, **100**, 23 (1953).
11) Y. Zyomoto and K. Higasi, to be published in this Bulletin. Further see Y. Zyomoto and K. Higasi, *Kagaku*, **26**, 638 (1956).
12) C. Ellis, *Proc. Roy. Soc.* (London), **212A**, 1 (1952).
* As the nature of Japanese coals is regarded to be particular as compared with European coals, this does not exclude the possibility that British bituminous coals have such graphite units.

*Sensitization by Bismuth of the Luminescence of Manganese and Samarium in Calcium Sulfide Phosphors**

By Shigeo SHIONOYA and Koh ERA

(Received February 27, 1957)

Abstract

Calcium sulfide phosphors doubly activated with bismuth as sensitizer and with manganese or/and samarium as activator were studied, in order to throw light on the sensitization mechanism of photoconductive phosphors. Their optical properties, reflection, excitation and emission spectra, were observed. A few estimations were done about the emission efficiency and the range of sensitization using these results. The facts directly found were that manganese is sensitized more efficiently than samarium, but the quenching takes place significantly in manganese itself, so that manganese is said to act, to some extent, as a killer. As the sensitization mechanism, the resonance transfer is considered to be more predominant than the photoelectron transfer. The contribution of the energy transport among the sensitizers is suggested. In the case of the coexistence of manganese and samarium, there will be no significant interactions between them.

Introduction

It has been proved that the mechanism of the sensitized luminescence in the non-photoconductive phosphors is explained by the resonance transfer of absorbed energy from sensitizer to activator[1,2]. In the photoconductive phosphors, however, the sensitization by a different mechanism has been considered to take place, such that electron and positive hole, released from the sensitizer by the photoabsorption, recombine at the activator, emitting its luminescence[3-5]. Hereafter this is called "photoelectron transfer". Then, the study of the real mechanism of the sensitization in the photoconductive phosphors is very interesting. In a study on the sensitized luminescence in zinc sulfide phosphors by one of the present writers[6,7], it has been concluded tentatively that the sensitization mechanism is the resonance transfer rather than the photoelectron transfer. The present study was undertaken to throw light on the sensitization mechanism in calcium sulfide phosphors, and here will be mentioned some results obtained until now.

Experimental

1. Preparation of Samples. — Bismuth as sensitizer and manganese or/and samarium as activator were selected. It has been known since earlier days that the sensitization takes place in these combinations[8,9]. The samples were prepared by mixing calcium oxide, excess sulfur, sodium sulfate as flux and the salts of activating impurities, and by firing the mixture for twenty min. at 950°C. The concentration of the sensitizer was constantly 10^{-4} (mole fraction relative to calcium, hereafter follow this), but that of the activator was varied from zero to 10^{-3}.

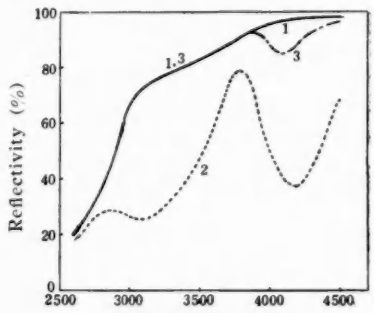

Fig. 1. Reflection spectra
(1) CaS (fired without any activating impurities)
(2) CaS:Bi(10^{-4})
(3) CaS:Mn(10^{-4})

* This work was read at the Symposium on Photochemistry held by The Chemical Society of Japan on September 29, 1956.

1) Th. P. J. Botden, *Philips Res. Rep.*, **7**, 197 (1952).
2) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
3) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals" (1940) p. 207.
4) M. Schön, *Z. Phys.*, **119**, 463 (1942).
5) H. A. Klasens, W. Ramsden and C. Quantie, *J. Opt. Soc. Am.*, **38**, 60 (1948).
6) S. Shionoya and K. Amano, *J. Chem. Phys.*, **25**, 380 (1956).
7) S. Shionoya, This Bulletin, **29**, 935 (1956).
8) S. Rothschild, *Phys. Z.*, **35**, 557 (1934); **37**, 757 (1936).
9) S. Makishima, Doctoral Thesis, University of Tokyo (1945).

2. Reflection Spectra.—As the samples were obtained only in the powder form, the reflection spectra were measured to learn the absorption characteristics. The measurement was done by means of "Shimazu's photoelectric spectrophotometer QB50". To eliminate the fluorescence (relatively weak in fact), a color filter, "Corning No. 9863", was inserted between the integral sphere and photomultiplier.

A part of the results is shown in Fig. 1. The long wavelength threshold of the fundamental absorption of the host crystal is located at 2500–2600Å. When bismuth is incorporated, a strong absorption appears in the long wavelength region beyond the above, the maxima of which are located at about 3100 Å and 4200 Å. The reflection spectrum due to bismuth corresponds to the spectrum of photoconduction[10]. The spectrum of the phosphor containing only manganese is very similar to that of the host crystal, but a weak absorption due to manganese appears at about 4100 Å. In the case of the phosphor containing only samarium, the spectrum is also very similar to that of the host crystal.

Reflection characteristics of doubly activated samples are very similar to that of the sample containing only bismuth; in other words their characteristics are determined only by bismuth. Small fluctuations were found in the result of each sample, but it seems to be dependent on the difference of the preparation condition, and not on the variation of the activator concentration. Then the absorption intensity in the series of samples containing a known amount of bismuth is almost constant irrespective of the activator concentrations. Therefore the emission efficiency should be in proportion to the number of emitted photons only. Then we will use the relative number of emitted photons instead of the emission efficiency, so as to compare the character of the samples with each other.

3. Excitation Spectra.—Since the intensity of emission excited by the light which passed through a monochromator was very weak, and further since it took a very long time to build up the emission to a saturated value, only the following method could be used. Phosphor powder was coated uniformly on a glass plate, and a photographic film was stuck on the other side of the plate sandwiching between the glass plate and film a gelatin filter which passes only the luminescence band to be measured. They were set at the focal plane of a usual quartz spectrophotometer. Then, the phosphor was irradiated for a long time (2-3 hr.) by the exciting light from a hydrogen discharge lamp. Therefore the results were not so precise and only qualitative.

A schematic figure obtained for bismuth emission of CaS:Bi is shown in Fig. 2. The excitation band for the activator, manganese or samarium, in the doubly activated phosphor is similar to that for bismuth in the singly activated phosphor. It has three peaks located at about 4200 Å (this is called B_1 band), 3100 Å (B_2 band) and 2500 Å

10) B. Gudden and R. W. Pohl, *Z. Phys.*, **3**, 98 (1920).

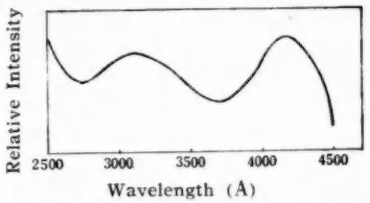

Fig. 2. Excitation spectra of CaS:Bi.

(H band), but the last one was not very clear.

Comparing these results with reflection spectra, it is concluded that B_1 and B_2 bands are due to the absorption of bismuth, while H band is due to that of the host crystal. Then it is concluded from the above facts that the luminescence of manganese or samarium is sensitized by bismuth in the spectral region from 3000 to 4500 Å. In the present study only the luminescence sensitized by bismuth will come into question.

4. Emission Spectra.—The measurement was done with a glass monochromator coupled with a photomultiplier. As the excitation source the 3650Å line of a high pressure mercury discharge lamp was employed for bismuth excitation, and the 2537Å line of a low pressure mercury discharge lamp for the host excitation. Some examples of the results are shown in Figs. 3 and 4. Although it is known that samarium emission spectrum consists of six groups of line spectra[9], only two groups located in the shorter wavelength region were measured here and each group was incapable of being resolved into lines because of the limitation of the abilty of the apparatus.

As shown in Fig. 3, the emission intensity of bismuth is weakened in proportion to the increase in the activator concentration, and further the degree of the decrease of bismuth emission in

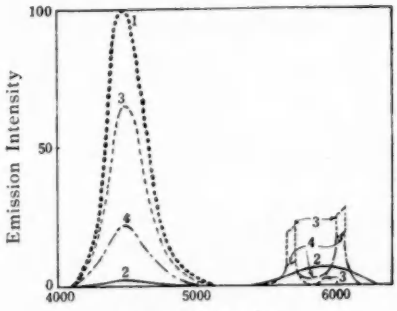

Fig. 3. Emission spectra under 3650 Å excitation. The ordinate is normalized by letting the bismuth emission peak of CaS:Bi be 100.

(1) CaS:Bi(10^{-4})
(2) CaS:[Bi(10^{-4})+Mn(10^{-3})]
(3) CaS:[Bi(10^{-4})+Sm(10^{-3})]
(4) CaS:[Bi(10^{-4})+Mn(3×10^{-3})+Sm(10^{-4})]

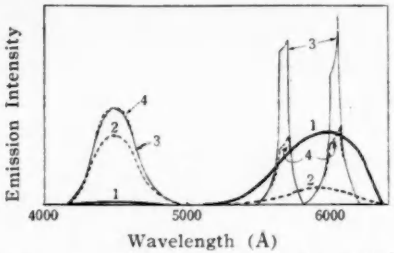

Fig. 4. Emission spectra under 2537Å excitation. The ordinate chosen arbitrarily.
(1) CaS:[Bi(10^{-4})+Mn(10^{-3})]
(2) CaS:[Bi(10^{-4})+Mn(10^{-5})]
(3) CaS:[Bi(10^{-4})+Sm(10^{-3})]
(4) CaS:[Bi(10^{-4})+Sm(10^{-5})]

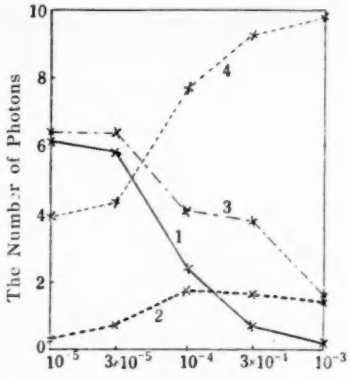

Fig. 5. The number of emitted photons for CaS:(Bi+Mn) series. The number for bimuth emission of CaS:Bi is put to be 10.
(1) Bismuth emission
(2) Manganese emission
(3) Sum of (1) and (2)
(4) The number of photons regarded to be transferred from bismuth to manganese, i.e. 10 minus (1)

Bi-Mn series is larger than in Bi-Sm series. These facts are due to the transfer of excitation energy absorbed in sensitizer to activator. In Bi-Sm series, samarium emission increases in proportion to its concentration, but in Bi-Mn series manganese emission does not become so strong in proportion to its concentration. This fact indicates that in Bi-Mn series the quenching of luminescence takes place in the manganese center after the energy transfer from bismuth to manganese.

These facts are made clearer by the estimation of the number of the emitted photons. The results of the estimation are shown in Figs. 5 and 6. The difference (N_d) of the numbers of photons emitted by bismuth between the case containing no activator and that containing it should be equal to the number of photons emitted by the activator. The ratio of the observed number of photons emitted by manganese to N_d in Bi-Mn series, which gives the efficiency of manganese emission, is shown in Table I. The efficiency is about 10–20%, indicating that the enormous quenching takes place in manganese activator itself. This is also understood by the fact that the curve (3) in Fig. 5 showing the sum of numbers of photons emitted by bismuth and manganese decreases with the increase in the manganese concentration. Then manganese may be considered, as a matter of fact, to act, to some extent, as a killer. Moreover, in the case of the higher concentration of manganese, the concentration quenching also takes place. In Bi-Sm series the value of the ratio N_d to the number of photons emitted by two groups of line spectra measured is always about 3.3, and as shown by the curve (3) in Fig. 6 the sum of the numbers of photons emitted by

TABLE I
EMISSION EFFICIENCY OF MANGANESE IN CaS: [Bi(10^{-4})+Mn]

manganese	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-3}	1×10^{-3}
efficiency (%)	8.3	17	23	17	14

TABLE II
VALUES OF z

A. CaS: [Bi(10^{-4})+Mn]					
manganese	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-4}	1×10^{-3}
z	5.1×10^{4}	1.8×10^{4}	1.4×10^{4}	8.8×10^{3}	3.9×10^{3}
B. CaS: [Bi(10^{-4})+Sm]					
samarium	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-4}	1×10^{-3}
z	2.8×10^{4}	9.1×10^{3}	4.4×10^{3}	1.5×10^{3}	5.0×10^{2}
C. CaS: [Bi(10^{-4})+Mn+Sm]					
manganese	1×10^{-4}	3×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-4}
samarium	3×10^{-5}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-3}
sum of manganese and samarium	1.3×10^{-4}	1.3×10^{-4}	2×10^{-4}	1.1×10^{-3}	1.1×10^{-3}
z	1.2×10^{4}	6.1×10^{3}	7.6×10^{3}	3.8×10^{3}	9.5×10^{2}

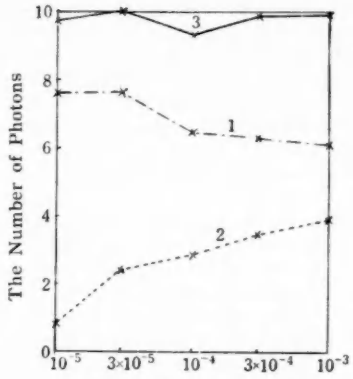

Fig. 6. The number of emitted photons for CaS:(Bi+Sm) series. The number for bismuth emission of CaS:Bi is put to be 10.
(1) Bismuth emission
(2) Samarium emission multiplied by 3.3
(3) Sum of (1) and (2)

bismuth and samarium is almost constant irrespective of the variation in the samarium concentration. Then it is considered that the quenching in the samarium activator does not take place, and that the above values of the ratio, 3.3, are really significant because only one third of the groups of the total ones of line spectra were measured. Comparing the decrease of bismuth emission in Bi-Mn series with that in Bi-Sm series, it is suggested that the ability of manganese to capture the excitation energy from bismuth is almost a hundred times that of samarium.

The emission spectra of the samples containing both manganese and samarium as activator are shown in Fig. 3. The emission intensity of bismuth is decreased with the incorporation of activators and the emissions of both activators appear.

TABLE III

THE NUMBER OF THE EMITTED PHOTONS UNDER 2537Å EXCITATION ARBITRARY UNIT)

CaS: Bi(10^{-4})	4.7×10^{2}
CaS: Mn(10^{-3})	4.1×10^{3}
CaS: Sm(10^{-3})	3.0×10^{3}

The ratio of the number of photons which is regarded to be transferred from bismuth to activator to that of photons emitted as bismuth luminescence, B, was calculated. Using B and the concentration of activator, z defined below which represents the range of sensitization can be calculated. z is defined as the number of lattice sites surrounding a given sensitizer, and it is assumed that if any one of these z sites is occupied by an activator, the sensitization can occur always with an efficiency of 100%, but that if none of them is occupied by an activator, the emission of the sensitizer itself is caused. Moreover it should be assumed that all activators are distributed at random over all the lattice sites and the transfer of energy between sensitizers never occurs. By means of the probability calculation[7],

$$z = -\frac{\log(1+B)}{\log(1-C_a)}$$

is obtained, where C_a is the mole fraction of activator. Although it is open to question whether the above assumptions are satisfied in this cases, at any rate z was calculated. The results are shown in Table II.

The emitted photons of each emission band under 2537Å excitation were calculated by means of Fig. 4. The results are shown in Table III. The unit was selected arbitrarily. Those of samarium are 3.3 times the value observed.

5. Emission under the Bismuth Excitation. —The measurement of perfect emission spectra under the excitation by each of the two peaks of the bismuth excitation band was impossible, because the suitable excitation source which is strong enough could not be obtained. Then, only the ratio of emission intensity of activator to that of sensitizer was possibly measured by means of separating each emission band with color filters. As an excitation source a $CaWO_4$-coated fluorescent lamp was employed with filter, Matsuda UV-D2, for B_1 excitation, and $Ca_3(PO_4)_2$: Tl-coated fluorescent lamp with nickel sulfate solution filter for B_2 excitation. For the selection of bismuth emission or activator's one, filter, Schott GG3 plus Matsuda VC-1, or Matsuda VO-2 were employed, respectvely.

The calculated ratios of the emission peak intensity of an activator to that of a sensitizer are shown in Fig. 7 for the three kinds of excitation. In Bi-Sm series, the ratios under two

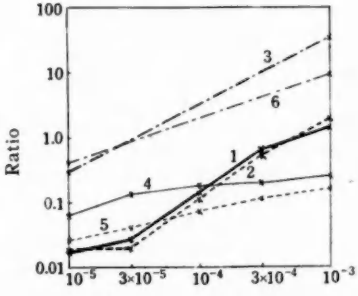

Fig. 7. The ratio of the emission peak intensity of activator to that of sensitizer under each excitation.
CaS:(Bi+Mn) series: (1) B_1 excitation (2) B_2 excitation (3) Host excitation
CaS:(Bi+Sm) series: (4) B_1 excitation (5) B_2 excitation (6) Host excitation

kinds of bismuth excitation are different from each other, and the sensitization efficiency under B_1 excitation is higher than under B_2, while in Bi-Mn series such a tendency is not found. In the case of the host excitation,the ratios in both sesies are so different from the case of bismuth excitation that it is suggested that there is a difference of luminescent mechanism between two cases.

Discussion

1. Sensitization Mechanism.—If the previous two assumptions on the calculation of z were realized truly, z should be constant irrespective of the variation of the activator concentration. In the present case, however, z decreases with the increase in the activator concentration, showing that the assumption will not be justified. Indeed, in the first place, it is considered that the assumption expressing no energy transfer between sensitizers is not realized, since the absorption spectrum of bismuth overlaps remarkably with its emission spectrum. The overlapping of an emission band with an absorption one is a necessary condition for the occurrence of resonance transfer, the probability of which is proportional to the degree of this overlapping. Then, it is considered that the sensitization in this case is caused by an energy transport, from sensitizer to activator, by which is meant a series of successive energy transfers such as sensitizer → sensitizer ⋯→ sensitizer → activator, and that the value of z indicates the mean path of this transport. The higher the concentration of the activator becomes, the more frequent the chance of energy transfer from sensitizer to activator is, so that the mean path of transport becomes shorter. From this fact, the decrease of z with the increase in the activator concentration previously mentioned will be explained.

Comparing z of Bi-Mn series with that of Bi-Sm series, it is shown that the values of both series tend to approach each other in the lower activator concentrations, but that in the higher concentrations the values of Bi-Mn series become larger than those of Bi-Sm by about one order of magnitude. As will be mentioned below, the range of interaction between sensitizers themselves is known to be larger than that between sensitizer and activator. In the lower activator concentration, therefore, it is considered that the path of energy transport determines mainly the range of sensitization. On the other hand, in the higher concentration the direct transfer between sensitizer and activator becomes predominant. The degrees of the sensitizer-activator interaction in both series might be different from each other by one order of magnitude—this will not be improbable. If so, the above facts will be reasonable.

It may be considered that the emission of the activator under the host excitation is caused by the recombination of photoelectron with hole both created by the photoabsorption. If so, it would be deduced reasonably, at first consideration, that the emission of the activator under the bismuth excitation band, in which photoconduction is known to occur, is also caused by the same mechanism. But there are some different points to be taken into consideration between the former the and latter case as mentioned below.

Referring to the knowledge about zinc sulfide crystal[11], it is considered that calcium sulfide crystal is an n-type semiconductor, i.e. the majority carrier is an electron. In the case of the host excitation, hole is created at the sulfur ion, one of the constituents of the host lattice. Therefore the probability of the creation of hole in the vicinity of any activator may be high enough in order that the activator can catch hole to emit luminescence, although the mobility of hole is rather low. But in the case of bismuth excitation, hole is formed at the ground state of bismuth, which is scattered throughout the whole crystal. This hole must be released thermally into the filled band in order that the sensitization can occur. Even if the probability of this release is large, the probability of the existence of an activator in the vicinity of any bismuth is so low, and the hole mobility is considered to be so low that the hole released from bismuth will scarcely be able to reach an activator to cause its luminescence. Then, although the electron migrates the sensitization by bismuth by means of the recombination of electron and hole will seldom take place.

On account of the above consideration, in the case of the crystal in which the mobility of one of the two charge carriers, electron and hole, is much higher than that of the other, it is expected that the sensitization by an incorporated impurity by means of the recombination hardly ever

11) G. F. J. Garlick and A. F. Gibson, *J Opt. Soc. Am.*, **39**, 935 (1949).

takes place, although under the host excitation this can be done. As already mentioned, it has been concluded that the impurity sensitization in the non-photoconductive phosphors is caused by the resonance transfer. Also in the photoconductive phosphors the sensitization by this mechanism will be able to occur. In this case the occurrence of the photoconductivity itself is not the essential condition. In the present case, for the reason which will be mentioned below, it is considered that the resonance transfer rather than the photoelectron transfer is the predominant mechnism.

The first reason is the fact that the nature of the emission under B_1 and B_2 excitation band are different from each other in the Bi-Sm series, whereas they are not so different in the Bi-Mn series. If photoelectron transfer were predominant, the difference would be the same grade in both series since the condition for the photoelectron transfer may be the same for both series. But, if the resonance transfer is predominant, this difference may be probable, because the absorption bands of samarium and manganese may be different from each other—the absorption character is the factor of resonance probability.

The second reason is mentioned below. Comparing the number of the photons emitted by manganese with that by samarium under 2537 Å excitation shown in Table III, both in the singly activated samples, it is considered that the capture cross sections of manganese and samarium for the electron and the hole are almost the same. In all cases except the sample of Bi-10^{-3} Mn, bismuth emissons are almost equal irrespective of the activator concentration, but the intensities of the activator emissions are lower than those of singly activated samples. Then it is considered that free electron and hole are captured preferentially by bismuth, and that in the process of luminescence the interaction between activator and sensitizer is very weak. But in the case of Bi-10^{-3} Mn this interaction seems to become fairly strong. Since, as mentioned above, the capture cross sections of manganese and samarium are not so different, it is most reasonable to consider, as the reason for this fact, that electron and hole are trapped at bismuth as the first step and then the resonance transfer occurs from bismuth to manganese. If the sensitization under bismuth excitation is due to the resonance transfer, this consideration is reasonably concluded. In all cases except Bi-10^{-3}Mn, because of the low activator concentration and the lower transfer probability, such a tendency scarcely appeared.

The third reason is that the estimated values of the range of sensitization, especially the relationships among them, are understood reasonably assuming the predominance of the resonance transfer. But, assuming the predominance of photoelectron transfer, these values are considered to be fortuitous. According to the theoretical treatment by Dexter[2], the sensitization range is the order of 10^1—10^3 lattice sites in the case of Bi-Bi type, and the order of 10^2 or 10 in the case of Bi-Mn or Bi-Sm. These are values for the typical cases, and considered to vary very much case by case. Now we are not speaking of the values themselves, but we are dis cussing relative tendencies. In the case of the lower activator concentration in which several successive steps of transfer may occur, the values lay in the order of 10^4. In the higher concentration region, even though the transfer between sensitizers may yet take place, the values were the order of 10^3—10^2. The difference of about one order between the Bi-Mn and Bi-Sm series will be probable on the premise that the resonance transfer is predominant and further the absorption band and the other factors are different between manganese and samarium.

So far, the distribution of activator and sensitizer has not been discussed, but implicitly assumed to be at random. The mode of distribution gives a serious influence on the sensitization efficiency. It is not fairly probable that the distribution is at random, but it is certainly considered that the activator and sensitizer form a kind of aggregate, and further that the aggregate states of Bi-Mn and Bi-Sm might be different from each other. If so, such a tendency will have the function to increase the sensitization efficiency, and true value of z will be smaller than those estimated here.

2. The Quenching in Manganese.—It is known that in manganese several excited states are involved, and that the states from which the luminescence is emitted is the lowest one[12]. In zinc sul-

12) C. C. Klick, *Brit. J. App. Phys.*, Sup. No. 4 ("Luminescence"), p. 74 (1955).

fide phosphors the absorption of manganese from the ground state to the lowest excited one occurs at about 5100Å[13]. Since the position of the emission peak of CaS : Mn is not so different from that of ZnS : Mn, the position of manganese absorption peak to the lowest excited state in the former is probably not so different from that in the latter. The maximum of bismuth emission in calcium sulfide phosphor is located at about 4500 Å, so that the resonance transfer to manganese will take place to its higher excited state rather than to the emitting one. It is considered that there are appreciable chances to cause the radiationless transition within manganese center during the stepping down from the higher excited state to the lowest one, and then this will be the cause of the quenching mentioned in Experimental 4. Moreover, in the case of the higher manganese concentration, the concentration quenching also seems to occur simultaneously.

13) R. H. Bube, *Phys. Rev.*, **90**, 70 (1953).

3. Interaction between Manganese and Samarium.—The phosphors containing both somarium and manganese as activators were prepared to investigate whether the interaction between them exists. But conclusive facts were not obtained, because the separation of their emission bands was impossible. From the results of calculation of z shown in Table II, it is seen in the comparison between two samples in which the sum of the concentration of two kinds of activator is the same that samples containing more manganese show larger z's. This also suggests that manganese catches more energy than samarium. Since z's in this case lie in the same region as in the case of singly activated ones, it may be concluded that a large interaction between manganese and samarium will not functions.

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Size and Structure of Commercial and Graphitized Carbon Blacks by Low-angle X-Ray Scattering and Colloid-chemical Methods

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Introduction

The measurement of size of colloidal perticles has been one of the most extensively investigated subjects in colloid science. Among various procedures for measuring the particle size, some methods have been adopted for routine industrial assessment of the colloidal products. However, little has been known on the mutual relationships between the values obtained by different methods, and the lack of knowledge in the correlation has lead to the equivocal elucidation of properties.

It seems very desirable, therefore, that some experiments to compare results from different methods for the same sample should be carried out.

Carbon black is an industrially available colloid, the properties of which have been investigated by means of various methods including electron-microscope[1], X-ray scattering[2-5], adsorption[1,6-16], or heat of wetting[10] methods, and distinguished, in most cases, in the spherical particle shape and absence of internal surface, in other words, an example of colloid of simple structure. The general properties and industrial applications of carbon blacks are to be referred to ref. (17).

In the present work, the average particle size values obtained from low-angle X-ray scattering, electron-microscope, molecular adsorption and heat of wetting with methanol for various carbon black samples have been compared and discussed. It appears that there is no need to assert the importance of the study of this kind to the industrial uses of the samples for rubber reinforcing filter, printing ink, coloring pigment and other miscellaneous purposes.

Description of Samples

Carbon Blacks.—The data characterizing fourteen carbon black samples investigated in the present work are summarized in Table I. These samples (five Japanese and nine American) appear to be representative of modern commercial carbon blacks with various general properties and uses. The designating symbols in the type of the samples are those widely adopted in the rubber industry and denote the process in manufacturing and uses: LCC, low color channel; FT, fine thermal; SRF, semi-reinforcing furnace; HAF, high abrasion furnace; HPC, hard processing channel; LFI, long flow impingement; MT, medium thermal; MAF, medium abrasion furnace; ISAF, impingement super abrasion furnace, SAF, super abrasion furnace. No pretreatment of extracting tarry matters attached to the carbon surfaces has been applied in this work.

Graphitized Carbon Black.—A gas thermal black, No. 1 in Table I, Tokyo Gas 300 (LCC), was subjected to heating and graphitization up to various temperatures.

To prepare the samples heated up to temperatures below 1000°C, a muffle furnace was employed. The carbon black was filled, in order to avoid oxidation by air, in a silica tube, which was thickly covered by asbestos to control the rate of heating, the temperature being measured by a thermo-couple inserted into the center of the

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1) R. B. Anderson and P. H. Emmett, *J. Appl. Phys.*, **19**, 367 (1948).
2) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).
3) M. H. Jellinek, E. Solomon and I. Fankuchen, *Ind. Eng. Chem., Anal. Ed.*, **18**, 172 (1946).
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10) G. Kraus, *J. Phys. Chem.*, **59**, 343 (1955).
11) F. E. Bartell and E. J. Miller, *J. Am. Chem. Soc.*, **45**, 1106 (1923).
12) H. A. Smith and R. B. Hurley, *J. Phys. Colloid Chem.*, **53**, 1409 (1949).
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16) J. Sameshima, H. Akamatu, K. Inouye, S. Kawamura, R. Matsuura and K. Tamaru, *Reviews of Modern Colloid Science*, **1**, 250 (1948).
17) W. R. Smith, "Encyclopedia of Chemical Technology," Vol. 3, The Interscience Encyclopedia, Inc., New York (1949).

TABLE I
DESCRIPTION OF CARBON BLACKS

No.	Carbon black	Type	Process	Manufacturer
1	Tokyo Gas 300	LCC	Gas thermal	Tokyo Gas Co.
2	Miike 20	FT	Gas thermal	Miike-gosei Co.
3	Asahi Carbon 40	SRF	Oil furnace	Asahi Carbon Co.
4	Seast 285	HAF	Oil furnace	Tokai Electrode Co.
5	Shoden Acetylene black	Acetylen black	Thermal	Showa-denko Co.
6	Micronex 2	HPC	Channel	Columbia Carbon Co.
7	Kosmos 15A	LFI	Channel	United Carbon Co.
8	Peerlees IIA	LFI	Channel	Peerless Carbon Black Co.
9	Thermax	MT	Gas thermal	Thermatomic Carbon Co.
10	Sterling S	SRF	Oil furnace	Cabot Inc.
11	Philblack A	MAF	Oil furnace	Phillips Petroleum Co.
12	Philblack O	HAF	Oil furnace	Phillips Petroleum Co.
13	Philblack I	ISAF	Oil furnace	Phillips Petroleum Co.
14	Philblack E	SAF	Oil furnace	Phillips Petroleum Co.

tube. The samples heated up to 420, 620 and 990°C were obtained at an average heating rate of 50± 10°C/min. The graphitized carbon black samples heated at temperatures above 1000°C were prepared by means of a Tammann furnace at the Omachi Factory of Showa Denko Co. Ltd. by the average rate of temperature rise of 50±10°C/min. up to 1300, 1700, 2100, 2420, 2630 and 3170°C, maintaining at the final temeratures for further 25 minutes.

Experimental Procedures

Low-angle X-ray Scattering.—Several workers[2-5] have applied the low-angle X-ray scattering method to derive the particle size of carbon blacks as a modern tool of particle size determination. Biscoe and Warren[2] employed a camera of 47.6 cm. specimen-to-film distance to record the scattering and calculated the particle size of three samples based on the Guinier's scattering intensity formula[18]. These authors showed the size in fair agreement with that obtained by the electron-microscopic method. Jellinek, Solomon and Fankuchen[3] have proposed a graphical method to obtain the particle size distribution from a single scattering recorded film and demonstrated it for a carbon black by means of a camera of specimen-to-film distance of 23.5 cm. This procedure was also applied to another sample by Turkevich and Hubbell[5] who used a camera of 70 cm. specimen-to-film distance with the Geiger counter to record the scattered X-rays. Brusset[4] also reported the size of five samples.

The calculation of particle size has been carried out by the theoretical functions relating the intensity of scattered X-ray to the scattering angles. Various functions have been proposed which differ in the treatments of the characteristics of the sample material, particle shape, particle distribution, etc. and the readers are raferred to excellent reviews by Yudowitch[19].

18) A. Guinier, *Ann. Phys.* **12**, 161 (1939).
19) K. L. Yudowitch, *Rev. Sci. Instr.*, **23**, 83 (1952); *Anal. Chem.*, **25**, 721 (1953).

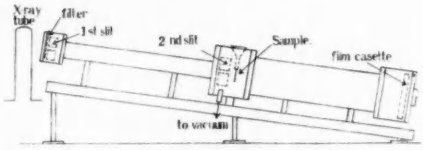


Fig. 1. A sketch of low-angle X-ray scattering camera.

The apparatus used in this work is a type of two-aperture collimating system camera. A sketch of the apparatus is drawn in Fig. 1. A first aperture of width a_1 and length b_1 is placed in metal block A. At a distence l from the first aperture is the second aperture in block B with width a_2 and length b_2. The scattering specimen is placed close to the second aperture. At a distance L from this specimen aperture is placed a cassette, in which the recording film is set, in the block C. The blocks A, B and C are tightly connected by means of rubber packings with two metal tubes to enable the inside of the apparatus to be evacuated. After Yudowitch[19], the intensity of the scattered rays, I, is considered to be

$$I \propto a_1 b_1 a_2 b_2 R^6 \rho^2 / l^2 L^2 \lambda^2 u^2, \tag{1}$$

where, R is the particle radius, ρ the electron density, λ the X-ray wave length and

$$u = 2\pi\varepsilon R/\lambda, \tag{2}$$

where, ε is the scattering angle. From Eqs. (1) and (2), it is noted that to give a strong intensity short length of l and L and a wide aperture as possible are recommended. On the other hand, Yudowitch[19] has given also the following conditions of camera geometry for the most intense usable data in the case of the slope analysis using the Guinier's equation:

$$l = L, \tag{3}$$

$$a_1 = 2\ a_2 = \lambda L \delta u / 4\pi R \tag{4}$$

$$b_1 = b_2, \tag{5}$$

and at a tolerable error,

$$a_1 < \lambda l / 3R, \tag{6}$$

where, δu denotes the collimation error. These relations imply that a long camera is useful to have the scattering pattern in a limited error and at the same time to employ wider apertures which are apparently easy to be made and operated. A sufficiently long specimen-to-film distance (L) is also necessary to assure a reasonable pattern. However, it is also clear that the long camera necessitates longer exposure time to obtain a scattering pattern on the film suitable to calculate the particle size. Fortunately, we have known that the average diameter of carbon blacks lies usually in the range of some hundreds angstrom, except very few thermal blacks with diameters of some thousands angstrom. The author has used the values of l and L of approximately 100 cm. (exactly, l is 1013 mm. and L is 993 mm.). From Eqs. (4), (5) and (6), the maximum value of a_1 may be calculated as shown in Table II in the case of the camera dimension described above and copper $K\alpha$ or chrome $K\alpha$ radiations. These values suggest that the exposure time may be shortened by employing a wider aperture system. In the present experiment, the dimentions of first and second appertures were taken as follows: (1) a_1 1.00 mm. and a_2 0.50 mm. for Cu $K\alpha$ radiation and (2) a_1 1.00 mm. or 0.50 mm. and a_2 0.50 mm. or 0.25 mm. for Cr $K\alpha$ radiation. In each condition, the relation (4) is applied. The height of apertures ($b_1 = b_2$) is 3.00 mm. In the case of (1), the samples with the average diameter less than 1000 Å. are expected to be analyzed, while in (2) the maximum diameter to be covered would be up to nearly 4000 Å. It is thus expected that almost all carbon black samples are tested by this camera in a reasonable accuracy. Other cautions to shorten the exposure have been taken in minimizing the absorption of X-rays by air in this very long (2 m.) camera by evacuating the whole path continuously during the exposure up to 10^{-2} mmHg and also the absorption by foil windows and filter. As is obvious in Fig. 1, the only source of absorption by camera window is the filter (Ni for Cu ray and V_2O_5 on Al foil for Cr ray) which is cemented with the first aperture and at the same time constitutes the window to keet the vacuum.

TABLE II

THE MAXIMUM WIDTH OF THE FIRST APEATURE IN A FUNCTION OF PARTICLE DIAMETER

Diameter, Å	a_1 maximum, mm.	
	Cu $K\alpha$ (1.54Å)	Cr $K\alpha$ (2.29Å)
100	10.4	15.5
500	2.08	3.10
1000	1.04	1.55
2000	0.52	0.78
5000	0.21	0.31

To reduce spurious radiations scattered from the apertures, the apertures have been designed to have a depth of 10 mm., so that a very clear-cut slit image is obtained in blank tests. A beam-stopper was used with the width of 2.5 mm. in the case of a_1 width 1.00 mm. or 1.4 mm. for a_1 0.50 mm.

The sample powder is extruded from a capillary in a small bar of 1 mm. diameter and set on a mount which is inserted inversely from the top of block B close to the second apperture and the sample mount is screwed in tightly to keep the vacuum.

By employing Cu radiation generated at 35 kV. and 20 mA. or Cr radiation at 35 kV. and 15 mA. Eastman-Kodak "No-screen" X-ray film, the exposure of 30 to 60 minutes was sufficient to give the suitable scattering patterns. A necessary by-earth voltage was applied to the filament of X-ray tube to reduce the focal spot width up to the same width of the first slit a_1; this procedure has resulted in strengthening the X-rays efficiently to pass through the camera. An example of the scattering patterns is shown in Fig. 2.

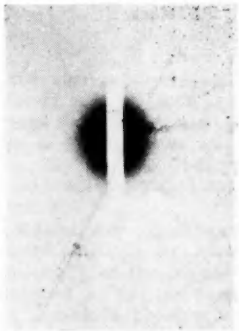


Fig. 2. An example of scattering pattern (×I). Sample: Philblack E.

The film obtained was micro-photometered by a reading photometer for each 0.25 mm. of film at a constant photometer condition. The calibration of the photographic density has been carried out by the graded-indensity scale method. The curves of the logarithm of measured (calibrated) intensity versus square of scattering angle (or of distance on film) showed a general shape as exemplified in Fig. 3. The average particle size was calculated from the straight part of the curve for each sample by use of the equation proposed by Guinier[18].

$$I = CWR^3 e^{-0.221k^2R^2}, \qquad (2)$$

where, I is the intensity, C a constant particular to the sample, W the mass of scattering elements, R the particle radius and k is $4\pi \sin(\varepsilon/2)/\lambda$. The Eq. (7) is changed to the following form:

$$\log I = A - BR^2f^2, \qquad (8)$$

where, A and B are constants and f is the distance on film of a scattering with intensity I.

It has been found the reproducibility of the experiment by these procedures is approximately 10% or, in most cases, with higher accuracy for the carbon blacks of less than 1000 Å. diameter.

X-Ray Powder Method.—The commonly used powder method was employed, using filtered

TABLE

No.	Carbon Black	Dia. from low-angle scattering, Å	Modal dia. by electron-microscope, Å	Iodine adsorption	
				Surface area, $m^2/g.$	Dia., Å
1	Tokyo Gas 300	732	500	37.8	848
2	Miike 20	1140	1120	8.77	3650
3	Asahi Carbon 40	1390	1020	7.75	4580
4	Seast 285	572	640	48.8	661
5	Shoden Acetylene black	1420	1250	22.3	1450
6	Micronex 2	576	250	47.3	713
7	Kosmos 15A	686	460	83.7	387
8	Peerless IIA	608	370	76.1	459
9	Thermax	1940(Cu) 4890(Cr)	3300	—	—
10	Sterling S	636	620	11.5	2730
11	Philblack A	620	450	17.4	1930
12	Philblack O	454	380	35.3	994
13	Philblack I	445	280	45.9	746
14	Philblack E	396	220	57.9	615

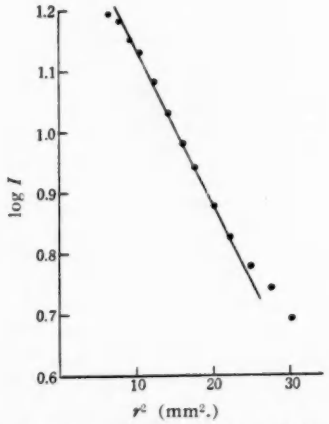


Fig. 3. An example of the relation between log I and r^2. Sample: Philblack E, I: absolute intensity, r: distance on film

copper $K\alpha$ radiation at 30 kV. and 20 mA. A calibrated camera (radius 45 mm.), powder specimen of 0.5 mm. diameter and Kodak "No-screen" films were used. The patterns of (002) and (100) indices were microphotometered for each 0.5 mm. of film and the crystallite dimensions were calculated for both patterns, Lc and La respectively, by the Laue-Brill procedure[20]. The crystallite dimension observed in carbon blacks implies the size of fundamental structural units of which the carbon black particle (a cluster of units) is constructed.

Electron-microscopic Method.—The enlarged electron-micrographs obtained for the samples have varying magnifying ratios between 14000 and 79000 according to the range of particle dimension. The sizes of numerous particles on the photographs were measured with the help of a magnifying glass and transparent scale, and the diameter of the most frequent counting (called the modal diameter) was determined.

Adsorption Measurements.—The most accurate method to evaluate the surface area will be the low-temperature adsorption method of nitrogen at liquid-air temperature[1,6-10] but a more feasible and rapid method of determining the specific surface area by adsorption of molecules from solutions has been applied to carbon blacks is frequently adopted. The compounds used for adsorbent are organic acids[11,12], iodine[13-16], diphenylguanidine[13], methylene blue[16], etc. In this work, the iodine and the methylene blue adsorption measurements were made which had been previously applied by the author to carbon black[16], coal[21] and coke[22].

The dried sample (0.5 g.) was added to 25 cc. of 0.1 N iodine solution at 25.0°C and the mixture stirred from time to time. The change in iodine concentration was determined after 1 hour. The specific surface area value could be derived from the adsorption per unit weight of sample, it being assumed that the adsorption is monomolecular and that the cross sectional area of adsorbed iodine molecule is 16.1 Å^2[23,24].

A 25 cc. portion of 0.4% methylene blue solution was added to 0.5 g. dried sample and stirred occasionally. The change in concentration after 24 hours at 25.0°C was determined with a photoelectric colorimeter. The specific surface area was again given from the adsorption data, the molecular area on solid surfaces being taken as $1.0\times10^3 m^2/g$[25]. The surface area value was then calculated in diameter by use of real density for each sample. The density was obtained picnometrically at 25.0°C with methanol after replacing

20) K. Inouye, H. Tani and M. Abiko, *J. Fuel Soc. Japan*, **32**, 292, 386 (1953).

21) K. Inouye, ibid., **29**, 112 (1950).

22) K. Inouye and H. Tani, *Fuel* (London), **34**, 356 (1955).

23) E. J. Mack, *J. Am. Chem. Soc.*, **47**, 2468 (1925).

24) L. H. Reyerson and A. W. Wishart, *J. Phys. Chem.*, **42**, 683 (1938).

25) F. Paneth and W. Thimann, *Ber.*, **57**, 1215 (1924).

III

Dye adsorption		Heat of Wetting			Crystallite dimensions	
Surface area, $m^2/g.$	Dia., Å.	Heat, cal./g.	Surface area, $m^2/g.$	Dia., Å	La, Å	Lc, Å
35.4	906	4.25	42.5	755	16.5	10.9
—	—	3.00	30.0	1070	15.4	12.0
—	—	—	—	—	17.5	11.4
53.3	606	2.83	28.3	1100	18.2	13.8
—	—	2.82	28.2	1150	43.1	24.8
61.0	553	—	—	—	16.5	14.3
189.	172	12.6	126.	257	19.5	10.1
120.	291	11.3	113.	309	20.9	12.4
—	—	—	—	—	21.5	11.9
17.8	1800	0.60	6.0	5350	17.3	14.2
27.1	1240	0.72	7.2	4680	20.7	13.6
50.3	689	1.95	19.5	1810	15.5	11.8
64.6	444	2.12	21.2	1660	18.2	11.1
81.7	365	3.47	34.7	1030	16.4	12.5

the occluded air by evacuating below 1 mmHg for several hours.

Heat of Wetting Method.—Kraus[10] has reported recently the heat of immersion of nine carbon black samples in water, methanol and *n*-hexane. The results was discussed in comparison with the specific surface area obtained by the nitrogen adsorption method at very low temperature and it was shown that the value of heat evolved by wetting the unit area varies with the nature of the sample, particularly the content of oxygenic radicals in carbon blacks.

In the present work, the heat-of-wetting measurements were made in order to derive the specific area on an assumption that the area per unit heat evolved is identical. The aparatus is a calorimeter comprising a Dewar flask with bakelite lid which is fixed to the flask by screws and supports all the working parts of the calorimeter: a stirrer which serves at the same time as a support of sample bulb, electrical heater and a Beckmann's thermometer to which a bulb-breaking device is attached. The Dewar vessel is immersed in a thermostat regulated at 25.0°C, which is situated in an air-bath controled at approximately 25°C. The construction and procedure are not very different from those proposed by earlier workers, in particular, by Griffith and Hirst[26]. Approximately 0.3-2.5 g. sample dried at 100-110°C for 1.5 hour and weighed in a thin-walled glass bulb, was evacuated at 10^{-4} mmHg for 5-6 hours at room temperature. After an equilibrium of temperature in Dewar vessel was attained, the bulb was broken in methanol (120 cc.) by a breaking device attached to the thermometer and the elevation of temperature was recorded at each 0.5 or 1 minute until when an equilibrium was again attained. The heat capacity was measured for each run by heating with known electrical energy supplied from a battery.

To derive the surface area from the heat-of-wetting, a value of area per unit heat of 10.0 m^2/cal. obtained by Bangham[27] and Maggs[28] for several carbonaceous substances was used.

The diameter was obtained from a specific surface area similarly as the absorption method by use of real density.

Electrical Resistivity Measurement.—The sample was dried at 110°C for 1 hour and the electrical conductivity of the compressed sample was then measured at various successive pressures with an apparatus constructed by Honda et at.[29]. The powder was placed in a steel tube and the pressure up to 3000 kg./cm^2 was exerted on it by a hydraulic system. The specific resistivity was plotted against $1/P$, $1/P^2$ or $1/\sqrt{P}$; where P denotes the pressure applied. The best linearlity has been found at the relations between the specific resistance and $1/\sqrt{P}$; the value of resistivity when P reaches infinity was taken as the characteristic value for each sample.

Results and Discussions

Carbon Blacks.—Table III summarizes the values of particle diameter obtained from the methods explained in the preceding section. The surface area and heat of immersion as well as crystallite dimension by powder method are also tabulated for reference.

The diameters obtained by low-angle scattering method and by electron-microscope are in fairly good agreement. However, it seems important to note that the value from low-angle scattering is, in most

26) M. Griffith and W. Hirst, "Proc. of Conf. on the Ultra-fine Structure of Coals and Cokes," British Coal Utilization Research Association, London (1944), p. 80.

27) D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc* (London), **A166**, 572 (1938).

28) F. A. P. Maggs, "Proc. of Conf. on the Ultra-fine Structure of Coals and Cokes," British Coal Utilization Research Association, London (1944), p. 95.

29) H. Honda, K. Ouchi and T. Toyoda, *J. Chem. Soc. Japan* (Pure Chem. Sect.), **76**, 364 (1955).

cases, larger than the value from the latter; the cause of this discrepancy may be due to some experimental errors, but it is also probable that the particles of carbon black have some connection with each other by means of bridges made of carboneceous substance with not a very different nature from the particles themselves, and the scattering dimension by X-ray is apparently larger than that expected by electron-micrographs in which all particles, even though they connect and form a skeleton or guitarshaped agglomerate, are recognized as separate particles piled up one above another. (See Fig. 4). Watson[30] has suggested that in

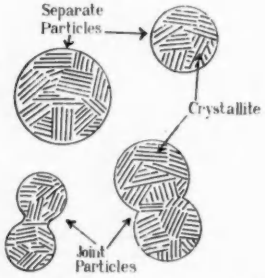


Fig. 4. Models of carbon black particles.

the electron-micrographs of shadowed carbon black particles some kinds of "essential" bridge forming between neighboring particles are observed. The possibility of the occurrence of the jointing particles as shown in Fig. 4 is also supported by the correlation between particles size and electrical resistance described in the next section. It is assumed from the results in Table III that the joining of this kind may be more noticeable in the samples with finer particle size, which showed larger discrepancy.

The particle diameter values obtained from adsoption methods and the heat-of-wetting measurement are somewhat parallel to those by X-ray and electron-microscopic method, but an exact comparison indicates that these colloid-chemical procedure, which are often employed in carbon black assessment, are by no means recognized as giving absolutely accurate results, and should be used only for a conventional qualitative comparison. As pointed out by Kraus[10], the adsorption or heat of immersion is largely affected by the chemical composition of reagents used as well as of carbon black itself, especially by the nature of surface of particles.

The crystallite size derived from line broadening of powder diffraction method gave almost similar dimensions of La (size in a-axis of hexagonal lamellae) and Lc (size in c-axis) ranging from approximately 10 to 20 Å, excluding only acetylene black which has more developed ultimate units. The concept of carbon black structure that the crystallites are piled in a very packed state so as to embrance no internal surface has been widely accepted (cf. Fig. 4). This is supported by the results of the present work (Table III) which show particle sizes from adsorption or heat of wetting methods, which will be able to measure the internal surface, are of approximately similar order as those from purely physical methods.

Graphitized Carbon Blacks.—The diameter revealed by low-angle method and the specific resistance method are tabulated in Table IV. The preparation of samples and measuring procedures are to be referred to the earlier descriptions.

As widely accepted, the crystallite dimensions increase with the elevation of graphitization temperature. Meanwhile, the size of particles, which are clusters of the ultimate unit crystallites, shows a very interesting change during the course of graphitization. On the other hand, the change in specific resistance is also particular. The relations between these three factors are illustrated in Fig. 5.

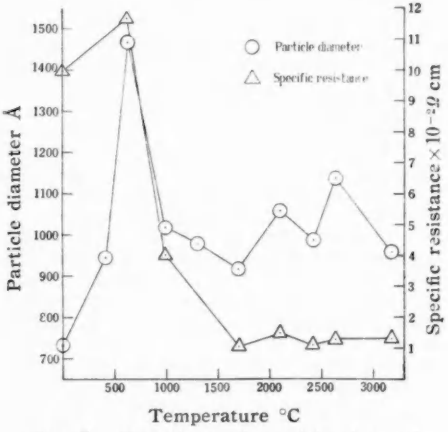


Fig. 5. Variations of particle size and specific resistance with treating temperature.

30) J. H. L. Watson, *J. Appl. Phys.*, **20**, 747 (1949).

Schaeffer et al.[31] have reported the electrical resistance variations with graphitization of some kinds of carbon black; they observed a sharp minimum of resistivity at approximately 1200°, followed by increase up to approximately 2500°C, and the second decrease at higher temperatures. An interpretation of these results was tried as the evolution of combined gaseous materials from the samples and the growth of the crystallite.

TABLE IV
PROPERTIES OF GRAPHITIZED BLACKS

Temp., °C	Diameter, Å	Dimension Å Lc	Crystallite La	Specific resistance, Ω cm.
Untreated	732	16.5	10.9	0.100
420	950	—	—	—
620	1470	21.1	14.1	0.117
990	1020	23.9	13.6	0.0410
1300	982	—	—	—
1700	920	50.8	36.9	0.0110
2100	1060	75.7	38.1	0.0158
2420	990	99.1	41.1	0.0119
2630	1140	47.8	50.0	0.0129
3170	960	61.9	40.8	0.0134

However, the present correlation between electrical resistance and particle diameter in Fig. 5 would suggest that the variation in resistivity is caused by a change in the state of agglomeration of the particles. As discussed in the earlier section, it has been indicated that the carbon black particles tend more or less to combine with each other to form conjoint particles that act as the scattering sources by X-rays and give large apparent diameter values. It is apparent that the conjoint particles shown in Fig. 4 can form only a loosely packed state and that such loose packing results in a difficulty of electrical conduction. The maxima in both electrical resistance and particle size at 620°C are most noticeable and it is expected that the carbonization of tarry substances on the surface of particles will play a part in forming a scaffolding particle system. The electron-micrographs also show somewhat agglomerated particle images for the samples treated at such temperature range. The linearity between particle size and resistance is also observed at higher temperature range in Fig. 5, but it seems that the formation of conjoint particles at higher temperature range than 1000°C is improbable. Another reason is therefore to be considered that the increase in particle size is also derived from extinction of smaller particles by heat treatment and vice versa. Based on the similar concept as suggested above, the increase in average particle size will cause a loosely packed state and have a high electrical resistance.

The author is pleased to acknowledge the helpful discussions relating to the present results by Prof. E. Suito (Kyoto Univ.) and Assis. Prof. K. Nagamatsu (Kyushu Univ.). His thanks are also due to Mr. R. Shinagawa (Resources Research Inst.) for help in designing the low-angle camera, Mr. H. Takahashi (Tokyo Univ.) for taking the electron micrographs, to Japan Carbon Black Association and Tokai Electrode Co. Ltd. for providing the samples examined and to Showa Denko Co. Ltd. for preparing the graphitized carbon black samples. The measurement of heat of wetting was carried out by A. Roppongi.

Resources Research Institute
Kawaguchi, Saitama

31) W. D. Schaeffer, W. R. Smith and M. H. Polley, *Ind. Eng. Chem.*, **45**, 172 (1953).

*Crystal Structure of a Monoclinic Form of Naphthazarin**

By Hideo WATASE, Kenji OSAKI and Isamu NITTA

(Received March 6, 1957)

Introduction

There have been reported three monoclinic modifications of naphthazarin ($C_{10}H_4O_2(OH)_2$)[1-3]. We obtained one of these, a needle crystal with metallic lustre, from acetic acid solution colored red. To this crystal Palacios and Salvia[1] have given the space group of C_{2h}^5 with two molecules in the unit cell**. Thus the molecule should be situated on a center of symmetry in the crystal lattice, while the usual chemical formula, 5,8-dihydroxy-1,4-naphthoquinone (I), has no center of symmetry. Thus further investigations are required to deal with the molecular structure.

(I)

Naphthazarin is similar to quinhydrone, the molecular compound of quinone and hydroquinone, in color, lustre and shape of the crystal, and has the same functional groups and planar form. From the result of X-ray analysis of quinhydrone[4], it is shown that the crystal has a very interesting structure, in which there is an anomalously short distance of 3.16 Å between the planes of successively overlying planar molecules as compared with the graphite interplanar value of 3.4 Å, and in which quinones and hydroquinones are linked linearly one after the other through the intermolecular hydrogen-bridges, these two interactions causing a layered structure to be formed. Therefore it becomes interesting to discover whether or not such special interactions are operative in the crystal structure of naphthazarin.

In this paper is given some information about the form of the molecule and the intermolecular interactions from two-dimensional X-ray analysis.

Unit Cell and Space Group

Oscillation, Sauter and Weissenberg photographs were taken about the needle axis (*a* axis) and another axis (*b* axis), using Cu K_α radiation. The photographs have shown a monoclinic lattice. The dimensions of the unit cell, containing two molecules, were as follows;

$a=3.74$, $b=7.63$, $c=14.53$ Å. $\beta=97.1°$.

From the Weissenberg photographs the intensities of reflexions were estimated visually, compared with a calibrated scale, multiple-film technique being used. Structure factors were deduced from these intensity data in the usual way.

At the first stage, the space group of $C_{2h}^5-P2_1/c$ was considered to be reasonable, since it appeared that no regular absences of reflexions were observed, except for $(0k0)$ when k is odd, and $(h0l)$ when l is odd. However, when the Weissenberg photograph of $(h0l)$ was examined carefully once more, some of the forbidden spectra were suspected to be appearing very faintly. On the long exposed oscillation photographs of the *a* axis, very weak but definite spectra of (101), (103), (103), (105) and (105) etc. were recognized. Therefore the symmetry element of glide plane is undoubtedly missing in the crystal.

In consequence, the space group is not $C_{2h}^5-P2_1/c$, but $C_2^2-P2_1$, although it may be said that the crystal has the symmetry of $C_{2h}^5-P2_1/c$ in a rough sense.

Application of Fourier-transform Method

It is reasonable to attempt the analysis of the structure of naphthazarin in assuming the space group of $C_{2h}^5-P2_1/c$, because the forbidden spectra are negligibly weak.

* The major part of this paper was read at the 6th Annual Meeting of the Chemical Society of Japan, April, 1953.

1) J. Palacios and R. Salvia, *Anales Soc. espan. fis. quim.*, **32**, 49 (1934).

2) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 1506 (1947).

3) O. Borgen, *Acta Chem. Scand.*, **10**, 867 (1956).

** According to the reports 1-3), the other two modifications have the space groups of C_{2h}^5, their unit cells containing two and four molecules respectively, and the volumes occupied by one molecule are nearly equal in the three modifications.

4) I. Nitta, H. Matsuda and K. Osaki, 2nd Intern. Congr. Cryst. (1951).

When the space group is C_{2i}^5 and the unit cell contains two planar molecules on its centres of symmetry, the best way of analysis is of application of the Fourier-transform method[5], and by this method the orientation of the reciprocal lattice to the molecule is found out easily.

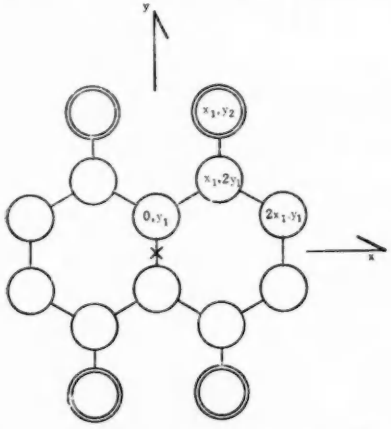


Fig. 1. Idealized molecular Model of naphthazarin for the Fourier transform. In this model $x_1=1.21$, $y_1=0.70$, $y_2=2.71$ Å, the atomic scattering factor of oxygen being assumed 3/2 of carbon. Single circles represent carbons and double circles oxygens.

An idealized molecular model was assumed as shown in Fig. 1. Then the Fourier transform of the molecule of naphthazarin was calculated, on the assumption of point-atoms, as follows (X, Y: the coordinates in reciprocal space):

$$T=2\cos 2\pi y_1 Y$$
$$+2\cos 2\pi(2x_1X+y_1Y)+2\cos 2\pi(2x_1X-y_1Y)$$
$$+2\cos 2\pi(x_1X+2y_1Y)+2\cos 2\pi(x_1X-2y_1Y)$$
$$+3\cos 2\pi(x_1X+y_2Y)+3\cos 2\pi(x_1X-y_2Y).$$

The transform map of Fig. 2 was obtained by the above calculations. From comparison between the observed structure factors and the transform map, the projection of the reciprocal lattice along the normal of the molecular plane could be determined without difficulty, as shown also in Fig. 2. The observed structure factors were fitted well with the values of the map in the following manner:***

Case ($0kl$);

$T_{0kl(\text{crystal})}=$
$T_{0kl(\text{molecule})}+\cos\pi(k+l)\times T_{0k\bar{l}(\text{molecule})}$.

Case ($h0l$);

directly on the map****.

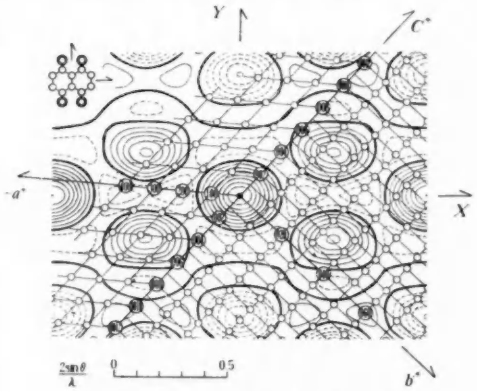


Fig. 2. The Fourier transform of naphthazarin showing the relation with the crystal reciprocal lattice. Solid, broad and broken contours are positive, zero and negative ones respectively, these intervals being of 2.

Thus the signs of the structure factors being given reliably, the Fourier summations of the electron-density projections along the a and b axes were then calculated, and by successive Fourier refinements the maps of Fig. 3 were derived after the signs of a few small structure factors had been changed. The atomic parameters obtained from the peaks of these maps are

(8.5/30, 9.8/60, 9.0/60),
(9.4/30, 16.2/60, 4.7/60),
(24.9/30, 29.1/60, 22.3/60),
(0.5/30, 26.3/60, 27.7/60) and
(4.3/30, 16.2/60, 29.2/60) for carbons,

and are

(25.3/30, 22.6/60. 18.3/60) and
(5.5/30, 9.5/60, 25.0/60) for oxygens.

In this stage, the reliability factors ($R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$) are 0.19 and 0.22 for ($0kl$) and ($h0l$) respectively, using the value of $B=5.0$ Å^2 as the temperature factor. In these calculations unobserved reflexions are omitted. The observed values of T_{hkl}, which are the absolute values of the structure factors divided by the atomic scattering factor[6] of carbon and the temperature factor, are listed in Tables I and II for comparison in the same scale with the values of the transform map.

5) G. Knott, *Proc. Phys. Soc.*, **52**, 229 (1940).

*** Because, in the present case, two molecules are in the unit cell and the space group is C_{2h}^5-$P2_1/c$.

**** $T_{h0l(\text{crystal})}=2T_{h0l(\text{molecule})}\times(\cos\pi l/2)^2$.

6) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

TABLE I

OBSERVED VALUES OF T_{0kl}

l \ k	0	1	2	3	4	5	6	7	8
0	—		− 5.8				+ 1.9		+ 4.0
1		+ 6.2	+ 1.4	+ 7.0	+ 8.5		− 3.5	− 7.6	− 4.0
2	+ 6.1	+ 2.4	− 5.0	+ 7.7	+ 9.4	− 1.9	− 8.2	+ 7.7	
3		− 5.7	− 5.7	+ 4.9	+ 8.8		+16.5	−14.7	− 7.5
4	− 4.6	+ 0.7	− 0.4	+ 4.6	+ 0.9	− 3.5	−17.0	+ 7.8	
5		+ 6.5	+ 4.2	−14.9			+13.3		− 8.3
6	+ 0.5	+ 7.6	+ 1.9	+10.1					
7		+ 5.0	+10.7	− 6.9	+ 1.8	+12.6	− 7.7		
8	− 3.4		+ 2.9	− 5.9	+15.9	+23.5			
9		− 1.2	− 1.4		+ 2.8	+ 3.7	+ 4.6		
10			− 4.9	− 3.5		+22.4			
11		− 9.8	+12.1						
12	+ 8.2	+12.0	−11.7						
13		−10.6							
14									
15									
16									

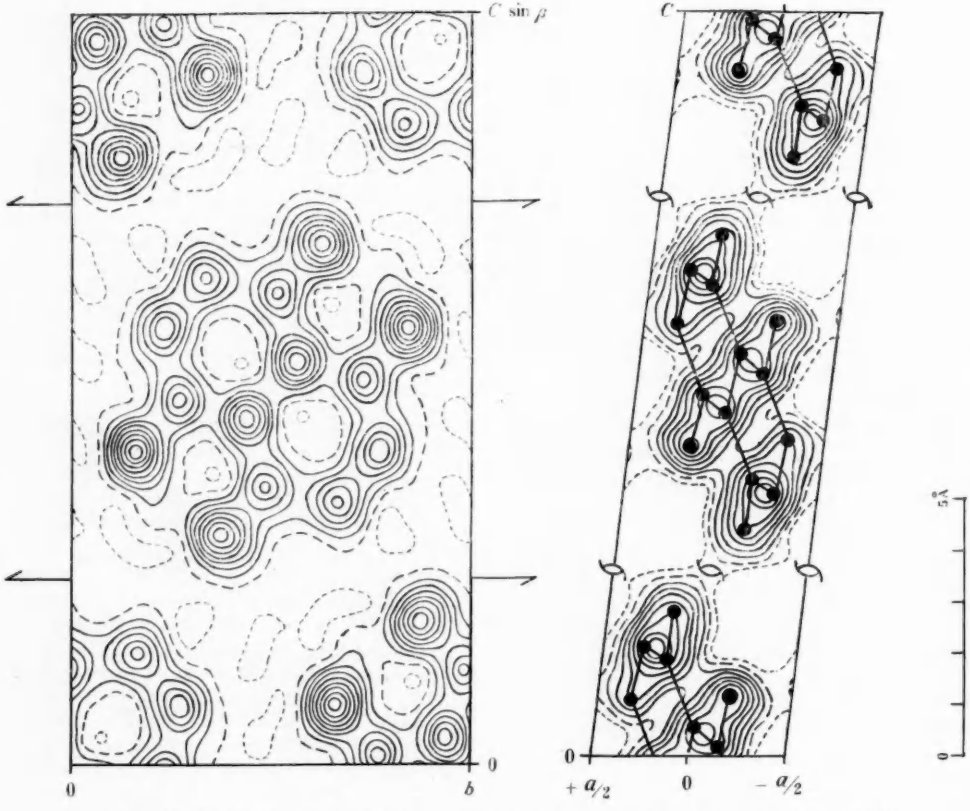


Fig 3. Electron-density projections along the a and b axes. Contours are drawn at equal intervals on an arbitrary scale for each map. Black circles in the b axis projection indicate the atomic positions.

TABLE II

OBSERVED VALUES OF $1/2\ T_{hol}$

The odd cases of l are omitted, the intensities of these reflexions being too weak to be estimated

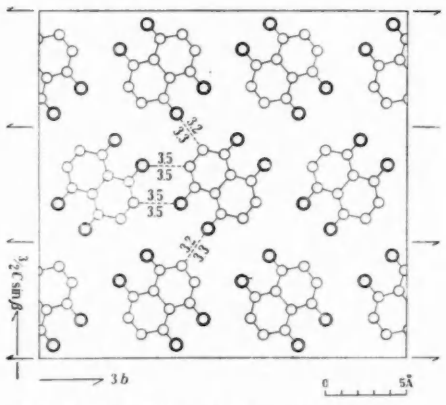
l \ h	4	3	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$
0	− 0.9	− 1.6	− 4.6	+ 5.4	—	+ 5.4	− 4.6	− 1.6	− 0.9
2		+ 0.9	+ 1.0	− 2.3	+ 3.2	+ 5.8	− 1.3	+ 1.1	+ 8.0
4			+10.9	+ 6.3	− 2.4	− 3.5	− 2.7	+ 0.6	+ 5.3
6			− 1.3	+ 3.6	+ 0.3	+ 0.2			
8			+ 0.4	− 0.5	− 1.5	+ 0.7	+ 2.3	− 6.2	− 1.6
10		− 8.2	− 3.0		+ 0.8	+ 1.7		− 6.9	
12			− 1.9	− 1.3	+ 3.5	− 6.6	− 1.9	+ 1.5	
14					+ 1.2	− 6.9	−12.1	− 3.8	
16						+ 1.2			

Discussion

Although the electron-density projection maps, shown in Fig. 3, are not very accurate, the maps show the principal feature of the crystal structure, and the interatomic distances derived from these maps give some information, since it may be considered that the degree of approximation is fairly high. The atomic distances between the molecules are shown in Figs. 4 and 5. The crystal structure is of a type entirely different from that of quinhydrone.

In the projection along the a axis, all the atoms are completely separated because of the very short period of this axis, each molecule being surrounded by six molecules two-dimensionally (Fig. 4). The molecular plane is inclined at only about 28° to the (100) plane.

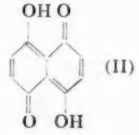
The projection along the b axis (Fig. 5) shows the feature of the planar molecules overlapping successively along the a axis (needle axis). The perpendicular distance between the planes of the molecules is found to be about 3.4 Å, the usual contact distance. There is no especially close approach as found in the structure of quinhydrone. This fact supports the discussion based on absorption spectra[7]; special interplanar interaction will not be operative in naphthazarine, since no such particular optical dichroism as shown by quinhydrone is detected.


3.5
3.5
3.5

That there is no intermolecular hydrogen bond, is also a point which differs from the case of quinhydrone. The intramolecular O—O distance is roughly 2.5 Å and six-membered hydrogen-bonded ring is considered to be formed here. The latter point is also revealed from the missing of the free O—H stretching vibration in the infrared spectra[8].

Quite recently, Borgen[3] has analysed the crystal structure of this modification to be of the space group of $C_{2h}^5-P2_1/c$, deriving the a axis electron-density projection by the use of the Patterson function, and has discussed some possible molecular models of centro-symmetry and molecular arrangements from this space group, since the usual chemical formula (I) is by itself incompatible with the space group. However, as we have pointed out above that the crystal has this symmetry only in a sense of approximation, it appears likely that those models and arrangements should be modified from this point of view, the formula (I) being not incompatible with the real crystal symmetry of $C_2^2-P2_1$.

In the classical sense the usual formula (I) and the centro-symmetric one (II) are to be considered as possible from the electron-density projection maps based upon $C_{2h}^5-P2_1/c$.



(II)

However it seems that the formula (II) is hardly suitable, since in such a manner of molecular grouping as shown by Figs. 4 and 5, it will be natural to suggest the crystal symmetry of $C_{2h}^5-P2_1/c$, if the molecule be of this formula. On the other side, from the stand point of the resonance stabilization, it may be said that the structure (II) is less stable than the formula (I).

Further, regarding the molecular structure, the spectra forbidden to the space group of $C_{2h}^5-P2_1/c$ are generally so weak that it may be supposed, as a probable explanation, that the molecule will have the structure considerably deviating from that corresponding in the classical sense to the formula (I) so as to approach the centro-symmetric form (II) to some extent. We can not of course conclude further what the real molecular structure is without more accurate determination of the atomic parameters. However, no further analysis is being attempted at present.

Finally, it is of interest to remark again that naphthazarin has at least three modifications in the region of ordinary temperatures.

We wish to express our thanks to Professor-Emeritus Chika Kuroda for supplying the specimen and to Mr. Yujiro Tomiie for continued interest.

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8) H. Brockmann and B. Franck, *Naturwiss.*, **42**, 45 (1955).

*Studies on Antibiotics and Related Substances. VI. Configurations of Isomeric O-Methylphenylserines and a New Route for the Synthesis of Chloramphenicol**

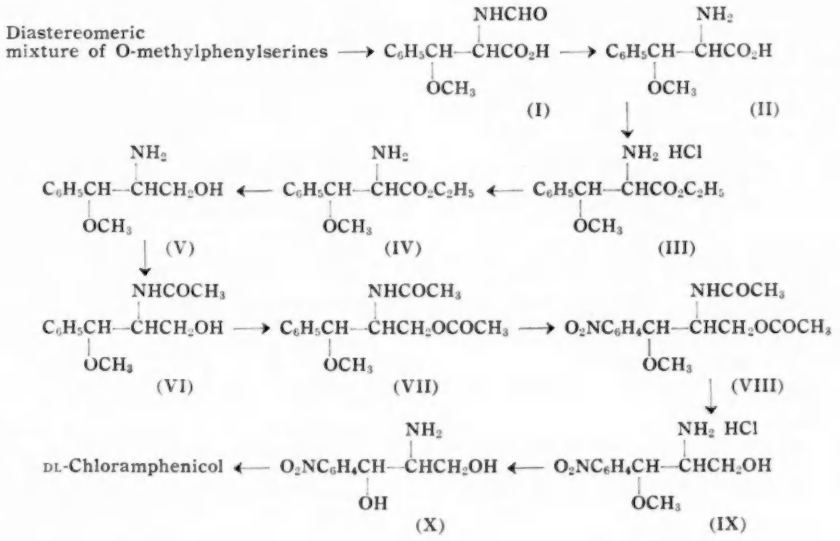
By Tetsuo SUAMI and Sumio UMEZAWA

(Received February 27, 1957)

In connection with synthetic studies on chloramphenicol in this Laboratory, the two diastereomers of O-methylphenylserine which were synthesized by Carter and Van Loon[1] became attractive as possible intermediates. The synthesis involved the methoxymercuration of cinnamic acid. In another paper West, Krummel and Carter[2] obtained one racemic form of α-bromo-β-methoxy-β-phenylpropionic acid by the reaction of methyl hypobromite with cinnamic acid in the presence of silver nitrate.

The present paper describes the studies on the configuration of diastereomeric O-methylphenylserines and the synthesis of DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol from one of the diastereomers. Synthetic studies concerning the configuration of the O-methylphenylserine (II), which was synthesized through methoxymercuration, is described first and followed by the synthesis of DL-chloramphenicol from II via DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol. Finally, studies on the other diastereomer (XI) of O-methylphenylserines is described.

Configuration of O-Methylphenylserine (II) Synthesized through Methoxymercuration.—The mixture of O-methylphenylserines melting at 215–219°C (dec.) was prepared by amination of the mixture of α-bromo-β-methoxy-β-phenylpropionic acids which was obtained by the synthetic route of Van Loon and Carter[3].



* Presented before the Division of Organic Chemistry at the Annual Meeting of the Chemical Society of Japan, at Kyoto University, April 3, 1956.

1) H. E. Carter and E. J. Van Loon, *J. Am. Chem. Soc.*, **60**, 1077 (1938).

2) H. D. West, G. S. Krummel and H. E. Carter, *J. Biol. Chem.*, **122**, 605 (1938).

3) E. J. Van Loon and H. E. Carter, *J. Am. Chem. Soc.*, **59**, 2555 (1937).

The mixture of O-methylphenylserines was formylated with concentrated formic acid to give a mixture of N-formyl derivatives, from which DL-threo-N-formyl-O-methylphenylserine (I) melting at 161–162°C was isolated as a single diastereomer by repeated recrystallization.

I was hydrolyzed with 1 N hydrochloric acid to yield DL-threo-O-methylphenylserine (II) melting at 218–220°C (dec.) in 89.3% yield. The N-benzoyl derivative of II which was obtained by benzoylation of II with benzoyl chloride in alkaline solution melted at 168–169°C.

II was treated with dry hydrogen chloride in absolute ethanol to give the ethyl ester hydrochloride (III) melting at 158–160°C. The free ethyl ester (IV) was obtained by bubbling ammonia through the ethereal suspension of III.

The ethyl DL-threo-O-methylphenylserinate (IV) was led to DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol and DL-chloramphenicol by the following procedure.

IV was reduced with hydrogen over Raney nickel catalyst to give DL-threo-O-methylphenylserinol (V) melting at 28–32°C in 41.9% yield. Acetylation of V with acetic anhydride at room temperature yielded N-acetyl derivative (VI) melting at 184–185°C. V was further acetylated by heating with acetic anhydride to yield N,O-diacetyl derivative (VII) melting at 120–121.5°C in 85.5% yield.

Nitration of VII with mixed acid under ice cooling yielded N,O-diacetyl-DL-threo-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol (VIII) melting at 80–82°C, which, on hydrolysis with 10% hydrochloric acid, yielded DL-threo-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol hydrochloride (IX) melting at 235–237°C (dec.).

Drastic hydrolysis of IX with 25% hydrochloric acid at 125–130°C in a sealed tube gave in a good yield a demethylated product (X), which did not depress the melting point of an authentic sample of DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol.

X was converted into N-dichloroacetyl derivative, viz. DL-chloramphenicol, which showed half the potency of the natural chloramphenicol against *Escherichia coli*. One can conclude, therefore, that a diastereomer of O-methylphenylserine which is obtained through methoxymercuration is of the threo configuration.

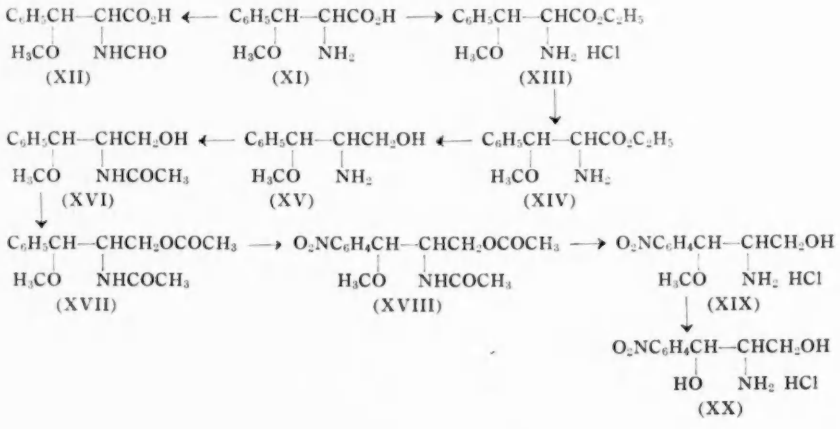
In the course of the above-mentioned investigation, we tried to demethylate the formyl derivative of O-methylphenylserine (I) by the action of concentrated hydrochloric acid. However, there was obtained 2-phenylnaphthalene, as would be expected from the report by Cater and Van Loon[1].

Derivatives of the Other Diastereomer (XI) of O-Methylphenylserine.—O-Methylphenylserine of m. p. 251–253°C (dec.) was prepared by the amination of α-bromo-β-methoxy-β-phenylpropionic acid by the method of Cater and co-workers[2].

The O-methylphenylserine afforded the corresponding N-formyl derivative (XII) melting at 149–150°C in a high yield by treatment with concentrated formic acid.

The O-methylphenylserine (XI) was treated with dry hydrogen chloride in absolute ethanol to yield the ethyl ester hydrochloride (XIII) melting at 179–181°C (dec.). The free ethyl ester was obtained by bubbling ammonia through an ethereal suspension of XIII.

Upon reduction of the ethyl ester (XIV)



with hydrogen over Raney nickel catalyst, the other diastereomer of O-methylphenylserinol (XV) was obtained as a syrup in 32.4% yield. When an ethereal solution of XV was saturated with dry hydrogen chloride, the crystalline hydrochoride of XV was obtained. This melted at 181–182°C. By benzoylation of XV with benzoyl chloride, N,O-dibenzoyl derivative melting at 160–161°C was obtained.

Acetylation of XV with acetic anhydride at room temperature yielded N-acetyl derivative (XVI) melting at 116–118°C. XVI was further acetylated by heating with acetic anhydride to yield N,O-diacetyl derivative (XVII) melting at 77–80°C.

Nitration of XVII with mixed acid under ice cooling yielded N,O-diacetyl-DL-erythro-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol (XVIII) melting at 150–151°C, which, on hydrolysis with 10% hydrochloric acid, yielded DL-erythro-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol hydrochloride (XIX) melting at 233–234°C (dec.).

Drastic hydrolysis of XIX with 25% hydrochloric acid at 125–130°C in a sealed tube gave DL-erythro-2-amino-1-*p*-nitrophenyl-1,3-propanediol hydrochloride (XX) melting at 209–210°C.

Thus, there is no contradiction in the assignment of the erythro configuration to the other O-methylphenylserine (XI).

Experimental

Amination of α-bromo-β-methoxy-β-phenylpropionic acid synthesized through methoxymercuration. — The diastereomeric mixture of α-bromo-β-methoxy-β-phenylpropionic acids was prepared through methoxymercuration by the route of Van Loon and Carter[3]. Thirty-seven grams of the bromo compounds were heated with 500 cc. of concentrated ammonia water at 90–100°C for 6 hr. in an autoclave. After being kept overnight at room temperature, the content was filtered and evaporated to dryness under reduced pressure. The residue was redissolved in a small portion of water, filtered and again evaporated under reduced pressure. The residue was triturated with acetone and allowed to stand with frequent shaking. The precipitate was collected and washed with acetone. The crude product of α-amino-β-methoxy-β-phenylpropionic acid melted at 215–219°C (dec.); yield 27 g. (97.0%).

N-Formyl-DL-threo-O-methylphenylserine (I).—A solution of 26 g. of the crude product of α-amino-β-methoxy-β-phenylpropionic acid in 150 cc. of 83% of formic acid was warmed to 45°C and 80 cc. of acetic anhydride was added with stirring. The temperature of the reaction mixture rose to, and was maintained at, 70–80°C for about 15 min.. Then, the solution was settled at room temperature for 3 hr. and evaporated to dryness under reduced pressure to yield a crystalline residue. Recrystallization from dilute acetic acid and then twice from hot water, gave colorless plates, m. p. 158–160°C; yield 5.5 g. (18.5%). A final recrystallization from hot water yielded colorless plates having a constant m. p. of 161–162°C; yield 4.9 g. (16.5%).

Anal. Found: N, 6.21. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28%. Completion of the remaining steps in the synthesis to DL-chloramphenicol proved this N-formyl derivative to be of the threo configuration.

DL-threo-O-Methylphenylserine (II). — Three and one-half grams of the above N-formyl derivative (I) was hydrolyzed with 40 cc. of 1 N hydrochloric acid on a boiling water bath for one hr.. The solution was neutralized with 10% sodium hydroxide solution to pH 6.5 and concentrated under reduced pressure until crystalline precipitate appeared. To the concentrate was added five volumes of absolute ethanol and the mixture was allowed to stand in a refrigerator overnight. The crystals were collected and washed with absolute ethanol; m. p. 218–220°C (dec.); yield 2.5 g. (89.3%). Recrystallization from water-ethanol gave colorless plates of O-methyl-DL-threo-phenylserine, m. p. 218–220°C (dec.).

Anal. Found: N, 7.19. Calcd. for $C_{10}H_{13}O_3N$: N, 7.18%.

N-Benzoyl-O-methyl-DL-threo-phenylserine. —To a solution of 0.5 g. of II in 5 cc. of 10% sodium hydroxide was added 0.5 cc. of benzoyl chloride under ice cooling with vigorous shaking. The mixture was kept at room temperature for 30 min. with occasional shaking. The solution was filtered to remove insoluble matter and then acidified with concentrated hydrochloric acid under ice cooling to yield colorless crystals, which were collected and washed with toluene, m. p. 166–167°C; yield 0.6 g. (78.1%). Two recrystallizations from methanol yielded colorless crystals of N-benzoyl-O-methyl-DL-threo-phenylserine, m. p. 168–169°C.

Anal. Found: N, 4.36. Calcd. for $C_{17}H_{17}O_4N$: N, 4.68%.

Ethyl O-Methyl-DL-threo-phenylserinate Hydrochloride (III).—A stream of dry hydrogen chloride was bubbled through a suspension of 4.0 g. of II in 40 cc. of absolute ethanol. After saturation, the mixture was settled at room temperature overnight, and then evaporated under reduced pressure to yield a crude ester hydrochloride; yield 5.2 g. (97.7%). Recrystallization from absolute ethanol-ether yielded colorless crystals of ethyl O-methyl-DL-threo-phenylserinate hydrochloride, m. p. 158–160°C.

Anal. Found: N, 5.22. Calcd. for $C_{12}H_{18}O_3NCl$: N, 5.39%.

Ethyl O-Methyl-DL-threo-phenylserinate (IV).—A vigorous stream of dry ammonia was passed through a suspension of 9.5 g. of III in 100 cc. of absolute ether for 20 min.. The ammonium chloride precipitated was removed and washed with absolute ether. The filtrate and washings were evaporated under reduced

pressure to yield a crude, pale-yellow oil of ethyl O-methyl-DL-threo-phenylserinate; yield 5.0 g. (61.2%).

DL-threo-2-Amino-1-methoxy-1-phenyl-3-propanol (V).—A solution of 5.0 g. of IV in 50 cc. of absolute ethanol was hydrogenated over 10 g. of Raney nickel catalyst[4] at 50–55°C for 5 hr. under an initial pressure of 120 atm.. The catalyst was removed by filtration, and the filtrate was evaporated under reduced pressure to yield a pale-yellow, oily residue; yield 3.0 g.. The residue was heated with 125 cc. of 0.1 N sodium hydroxide solution for 2 hr. in order to hydrolyze any unchanged ester. The alkaline solution was extracted five times with ethyl acetate under ice cooling. The combined ethyl acetate extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield crude crystals of DL-threo-2-amino-1-methoxy-1-phenyl-3-propanol (V), m. p. 28–32°C; yield 1.7 g. (41.9%).

On bubbling dry hydrogen chloride into the ethereal solution of V, colorless crystals of crude hydrochloride was obtained; m. p. 164–166°C. Two recrystallizations from ethanol-ether gave pure crystals of the hydrochloride of V, m. p. 168–169°C.

Anal. Found: N, 6.21. Calcd. for $C_{10}H_{16}O_2NCl$: N, 6.43%.

N, O-Dibenzoyl-DL-threo-2-amino-1-methoxy-1-phenyl-3-propanol.—To a solution of 0.2 g. of V in 2.0 cc. of dry pyridine was added 0.3 cc. of benzoyl chloride and the mixture was allowed to stand in an ice bath for 1 hr. with occasional shaking. Cold water was added to the solution and the crystals formed were collected and washed with 2% sodium carbonate solution, 1% hydrochloric acid and finally with cold water. Recrystallization from methanol gave colorless needles, m. p. 138–139°C; yield 0.4 g. (92.9%). Further recrystallization from methanol gave an analytical pure sample of the N,O-dibenzoyl derivative of V, m. p. 139–140°C.

Anal. Found: N, 3.68. Calcd. for $C_{24}H_{23}O_4N$: N, 3.60%.

N-Acetyl-DL-threo-2-amino-1-methoxy-1-phenyl-3-propanol (VI).—To a solution of 0.2 g. of V in 2.0 cc. of ether was added 0.8 cc. of acetic anhydride with stirring at room temperature. Crystals formed were collected and washed with ether to yield colorless crystals, m. p. 178–180°C; yield 0.2 g. (81.0%). Recrystallization from hot water gave colorless needles of N-acetyl derivative of V, m. p. 184–185°C.

Anal. Found: N, 6.12. Calcd. for $C_{12}H_{17}O_3N$: N, 6.27%.

N, O-Diacetyl-DL-threo-2-amino-1-methoxy-1-phenyl-3-propanol (VII).—V (0.8 g.) was heated with 6.0 g. of acetic anhydride on a boiling water bath for one hr.. The solution was concentrated under reduce pressure to yield crystals, which were washed with ether, m. p. 119–121°C; yield 1.0 g. (85.5%). Two recrystallizations from acetone gave colorless plates of the N,O-diacetyl derivative of V, m. p. 120–121.5°C.

Anal. Found: N, 5.25. Calcd. for $C_{14}H_{19}O_4N$: N, 5.28%.

N, O-Diacetyl-DL-threo-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol (VIII).—To 1.3 g. of VII was added 5.0 cc. of a mixture (1 : 1) of concentrated nitric acid (sp. gr. 1.38) and sulfuric acid (sp. gr. 1.84) under ice cooling and shaking. After 15 min. the mixture was kept at room temperature for 20 min. quenched on ice and then immediately neutralized with sodium bicarbonate. The mixture was extracted five times with ethyl acetate and the combined extract was washed with cold water, and dried over anhydrous sodium sulfate. Evaporation under reduced pressure yielded pale-yellow crystals of the nitro derivative of VII, m. p. 80–82°C; yield 1.4 g. (92.2%).

Anal. Found: N, 9.22. Calcd. for $C_{14}H_{18}O_6N_2$: N, 9.03%.

DL-threo-2-Amino-1-methoxy-1-*p*-nitrophenyl-3-propanol Hydrochloride (IX).—A portion of 1.4 g. of VIII was hydrolyzed with 10 cc. of 10% hydrochloric acid on a boiling water bath for one hr. The hydrolysate was washed twice with ether and and evaporated to dryness under reduced pressure. The crystalline residue was recrystallized from dilute hydrochloric acid to yield colorless crystals of DL-threo-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol hydrochloride, m. p. 235–237°C (dec.); yield 1.1 g. (92.5%). When dried in a "pistol" the compound was unstable and colored.

Anal. Found: N, 9.92. Calcd. for $C_{10}H_{15}O_4N_2Cl$: N, 10.67%.

DL-threo-2-Amino-1-*p*-nitrophenyl-1,3-propanediol (X).—A mixture of 1.1 g. of IX and 12 cc. of 25% hydrochloric acid was placed in a sealed tube and heated at 125–130°C for 4 hr.. The contents were diluted with water, decolorized with active carbon, and then concentrated under reduced pressure to give a crystalline residue; yield 1.0 g. The residue was dissolved in 3.0 cc. of water, cooled with ice, and rendered alkaline with 10% sodium hydroxide solution to pH 10. The free base in the mixture was extracted with ethyl acetate repeatedly and the combined extract was concentrated under reduced pressure to yield 0.7 g. (82.4%) of a crystalline residue, which was recrystallized several times from hot water to give colorless crystals of m. p. 139–140°C; yield 0.3 g. (35.5%). Admixture with DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol synthesized by the route of Controulis et al.[5] caused no depression in the melting point.

X was converted into the N-dichloroacetamide of m. p. 149–150°C by heating with methyl dichloroacetate. The antibacterial activity of the product, viz. DL-chloramphenicol, was 49.7% that of natural chloramphenicol by a cylinder plate assay (test organism E. coli).

2-Phenylnaphthalene.—A mixture of 1.0 g. of I and 10 cc. of 20% hydrochloric acid was

4) Organic Syntheses, **21**, 15 (1940).

5) J. Controulis, M. C. Rebstock and H. M. Crooks, Jr., *J. Am. Chem. Soc.*, **71**, 2463 (1949).

placed in a sealed tube and heated at 115–120°C for 4hr.. The contents were extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and then concentrated under reduced pressure to yield a yellow crystalline residue; yield 0.4 g. (87.5%). The product was recrystallized from methanol to give pale yellow crystals of m. p. 101–102°C. Admixture with an authentic sample of 2-phenylnaphthalene caused no depression in the melting point.

N-Formyl-DL-erythro-O-methylphenylserine (XII).—The other diastereomer (XI) of O-methylphenylserine which melts at 251–253°C (dec.) was prepared by the method of Carter et al[1,2].

One gram of XI was dissolved in 6 cc. of 83% formic acid, warmed to 45°C and then 3.0 cc. of acetic anhydride was added under shaking. The temperature of the reaction mixture was maintained at 70–80°C for 15 min.. Evaporation under reduced pressure gave a crystalline residue, which was recrystallized from 2 cc. of hot water to give crystals of m. p. 143–146°C; yield 0.8 g. (70.0%). Repeated recrystallization from hot water gave the N-formyl derivative of single diastereomer of O-methylphenylserine, m. p. 149–150°C.

Anal. Found: N, 6.32. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28%.

Ethyl DL-erythro-O-Methylphenylserinate Hydrochloride (XIII).—A stream of dry hydrogen chloride was bubbled into a suspension of 10 g. of O-methylphenylserine (XI) in 150 cc. of absolute for ethanol for 1.5 hr.. After saturation, the solution was allowed to stand overnight at room temperature and evaporated under reduced pressure to yield a crystalline residue; 13.0 g. (97.7%). Recrystallization from absolute ethanol-ether gave colorless needles of the ester hydrochloride of XI, m. p. 179–181°C (dec.).

Anal. Found: N, 5.44. Calcd. for $C_{12}H_{15}O_3NCl$: N, 5.39%.

Ethyl DL-erythro-O-Methylphenylserinate (XIV).—A vigorous stream of dry ammonia was passed through a suspension of 13 g. of the hydrochloride (XIII) in 150 cc. of absolute ether for 20 min.. After-treatment was carried out just as described above in the preparation of IV. The yield of crude, pale-yellow oil was 10.0 g. (89.3%).

DL-erythro-2-Amino-1-methoxy-1-phenyl-3-propanol (XV).—A solution of 9.5 g. of XIV in 100 cc. of absolute ethanol was hydrogenated with 10 g. of Raney nickel catalyst[4] at 45–52°C and 120 atm. for 4 hr.. After-treatment was carried out just as described above in the preparation of V to yield a crude product of XV, a pale-yellow oil; yield 2.5 g. (32.4%).

Dry hydrogen chloride was bubbled through the ethereal solution of the crude syrup of XV to yield colorless crystals, which were collected and washed with dry ether and acetone; m. p. 175–177°C. Three recrystallizations from methanol-ether gave an analytical sample of the hydrochloride of XV, m. p. 181–182°C.

Anal. Found: C, 54.83; H, 7.13; N, 6.29. Calcd. for $C_{10}H_{16}O_2NCl$: C, 55.15; H, 7.40; N, 6.43%.

M. p. reported by Tatsuoka et al[6]. is 182–183°C.

N, O-Dibenzoyl-DL-erythro-2-amino-1-phenyl-3-propanol.—To a solution of 0.2 g. of the crude syrup of XV in 2.5 cc. of pyridine, was added 0.3 cc. of benzoyl chloride under ice cooling and shaking. The solution was cooled in an ice bath for 1 hr. and then allowed to stand at room temperature for 30 min.. Cold water was added to the solution to yield a crystalline precipitate, which was collected and washed with 2% sodium bicarbonate solution, 1% hydrochloric acid and finally with cold water. Three recrystallizations from methanol gave colorless needles of N, O-dibenzoyl derivative of XV, m. p. 160–161°C; yield 0.3 g. (69.8%).

Anal. Found: N, 3.71. Calcd. for $C_{24}H_{23}O_4N$: N, 3.60%.

M. p. reported by Tatsuoka et al[6]. is 157–158.5°C.

N-Acetyl-DL-erythro-2-amino-1-methoxy-1-phenyl-3-propanol (XVI).—To a solution of 2.2 g. of XV in 10 cc. of ether was added 4.0 cc. of acetic anhydride at room temperature. After-treatment was carried out just as described above in the preparation of VI to yield a crude product of XVI, m. p. 115–117°C; yield 2.1 g. (77.5%). Recrystallization from ethyl acetate gave colorless crystals of XVI, m. p. 116–118°C.

Anal. Found: N, 6.05. Calcd. for $C_{12}H_{17}O_3N$: N, 6.27%.

N, O-Diacetyl-DL-erythro-2-amino-1-methoxy-1-phenyl-3-propanol (XVII).—A 1.0 g. sample of XVI was heated with 6.0 cc. of acetic anhydride on a boiling water bath for one hr. The solution was concentrated under reduced pressure to yield crude crystals, m. p. 77–80°C; yield 1.2 g. (100.9%).

N, O-Diacetyl-DL-erythro-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol (XVIII).—To 1.0 g. of XVII was added 5.0 cc. of a mixture (1 : 1) of concentrated nitric acid (sp. gr. 1.38) and sulfuric acid (sp. gr. 1.84) under ice cooling and shaking. After-treatment was carried out just as described above in the preparation of VIII to yield a crude product of XVIII, m. p. 122–140°C; yield 1.2 g. (102.6%). Two recrystallizations from ethanol gave colorless crystals of XVIII, m. p. 150–151°C.

DL-erythro-2-Amino-1-Nethoxy-1-*p*-nitrophenyl-3-propanol Hydrochloride (XIX).—A portion of 1.1 g. of XVIII was hydrolyzed with 10 cc. of 10% hydrochloric acid on a boiling water bath for one hr.. The hydrolysate was evaporated to dryness under reduced pressure. The crystalline residue was recrystallized from water to yield colorless crystals of DL-erythro-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol hydrochloride, m. p. 233–234°C. (dec.); yield 0.7 g. (75.2%).

6) S. Tatsuoka, M. Miyamoto, T. Kinoshita, R. Nakamori and S. Kimata, *J. Pharm. Soc. Japan*, **71**, 608 (1951).

Anal. Found: N, 10.37. Calcd. for $C_{10}H_{15}O_4N_2Cl$: N, 10.67%.

M. p. reported by Tatsuoka et al[6]. was 232°C.

Admixture with DL-threo-2-amino-1-methoxy-1-*p*-nitrophenyl-3-propanol hydrochloride (IX) caused a depression in the melting point.

DL-erythro-2-Amino-1-*p*-nitrophenyl-1, 3-propanediol Hydrochloride (XX).—A mixture of 0.7 g. of XIX and 12 cc. of 25% hydrochloric acid was placed in a sealed tube and heated at 125–130°C for 4 hr.. The contents were diluted with water and filtered. Then the filtrate was concentrated under reduced pressure to give a crystalline residue. The residue was recrystallized from methanol to yield colorless crystals, m. p. 207–209°C; yield 0.2 g. (30.3%).

Recrystallization from methanol yielded colorless crystals of DL-erythro-2-amino-1-*p*-nitrophenyl-1,3-propanediol hydrochloride, m. p. 209–210°C..

Anal. Found: C, 43.41; H, 5.04; N, 11.09. Calcd. for $C_9H_{13}O_4N_2Cl$: C, 43.42; H, 5.23; N, 11.26%.

Controulis et al[5]. reported DL-erythro-2-amino-1-*p*-nitrophenyl-1,3-propanediol hydrochloride of m. p. 212–214°C.

Summary

(1) DL-threo-O-Methylphenylserine has been isolated through its N-formyl derivative from the diastereomeric mixture of O-methylphenylserines which was prepared by the route of Van Loon and Carter[3].

(2) DL-threo-O-Methylphenylserine has been led to DL-threo-2-amino-1-*p*-nitrophenyl-1,3-propanediol and further to DL-chloramphenicol.

(3) The other diastereomer of O-methylphenylserine (m. p. 251–253°C) has been led to DL-erythro-2-amino-1-*p*-nitrophenyl-1,3-propanediol hydrochloride.

(4) Several derivatives of the diastereomers of O-methylphenylserine and O-methylphenylserinol have been described.

The authors are indebted to Mr. S. Nakada of this Laboratory for the microanalytical data.

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Dielectric Studies on Colloidal Solutions. IV. The Dielectric Constant of the Solutions of Long-chain Amine Hydrochlorides

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(Received March 18, 1957)

In the first paper of this series[1], the result of the measurement of high-frequency conductivities of aqueous solutions of colloidal electrolytes has been reported; the measurement of the dielectric constants of their solutions, which is reported in this paper, must also be an important approach to the understanding of the nature of the electrolytes.

Experimental

Procedure.—The measurement of the dielectric constant (D. C.) at 2 Mc./sec. has been carried out by means of the heterodyne beat method. The main part of the apparatus consists of two separate oscillators, one of which is held at a frequency of 2 Mc./sec. by the vibration of a quartz crystal and the other is adjusted by varying its capatity to give a frequency different by a constant amount from that of the former oscillator. A liquid cell is incorporated into the circuit of the latter oscillator. The adjustment of the frequency of the latter oscillator is performed by the addition of a 700 cycles/sec. tuning-fork oscillator to the apparatus, and against that oscillator the beat note is balanced by a cathode-ray oscilloscope. Each electrical component is enclosed in an earthened metal box.

The precision condenser consists of two variable air condensers; the one has a working range of 100 pF traversed in 25 turns and the other that of 11.25 pF traversed in 90 turns. The division of the former condenser is 1/100 turns and that of the latter is 1/50 turns.

The measurement of D. C. at 30 Mc./sec has been carried out by the resonance method used for the measurement of the high-frequency conductivity[1]. The resonance point is obtained by determining the whole resonance curve of the resonant circuit containing the measruring cell, so that the precision of the resonance point is sufficiently accurate.

1) M. Shirai and B. Tamamushi, This Bulletin, **28**, 545 (1955).

The cell used is constructed of parallel plates of platinum enclosed in a glass vessel which is immersed in a constant temperature bath of toluene, and fixed at a definite position. The cell constant is determined by using distilled water as the standard whose D. C. is taken to be 73.02 at 40°C[2].

The electrical conductivity has been measured with the impedance bridge used in the previous work[3].

Materials.—Hexadecyl- and octadecylamine hydrochloride were prepared from the corresponding amines (Armour & Co., U. S. A.) by the method given in the previous paper[4].

Ethanol was distilled over calcium oxide: b. p. 78.3°C.

Benzene was purified from a commercial sample by washing with sulfuric acid and then with water, followed by drying over calcium chloride and distillation: b. p. 80°C.

The water used is the conductivity water distilled in an nitrogen atomsphere.

Results and Discussion

1) **Electrode polarization**—In measuring D. C. of a conductive medium, the electrode polarization often causes a serious error. This error is inversely proportional to the square of the frequency at which the measurement is made[5]. The error in the present investigation is expected to be very small as the frequency employed is high, being 2 Mc./sec. In reality, D. C. of aqueous solutions of potassium chroride at various concentrations obtained has been found nearly constant as shown in Table I. A little increase in D. C. at higher concentrations may be interpreted in terms of Debye-Falkenhagen's effect of potassium chloride. Thus, it is conceivable that the values of D. C. obtained are free from the error due to the electrode polarization at the range of concentration and at the frequency at which the measurement has been carried out.

TABLE I

DIELECTRIC CONSTANT OF AQUEOUS SOLUTION OF POTASSIUM CHLORIDE (temp 40°C)

conc. (mole/l.)	ε(2Mc./sec.)
0.0001	73.02
0.0002	73.02
0.0003	73.03
0.0005	73.05
0.0008	73.21
0.001	73.45

2) **D. C. of aqueous solutions of salts.**—The result of the measurement of D. C., ε, and the equivalent conductivity (E. C.), Λ, of aqueous solutions of hexadecyl- and octadecylamine hydrochloride is shown in Table II and in Fig. 1, where the relative increase of D. C. or E. C. is plotted as ordinate against the square root of the concentration of amine salts as abscissa. The relative increase in D. C. is there expressed by

$$100\,\frac{\varepsilon-\varepsilon_0}{\varepsilon_0}$$

in which ε and ε_0 denote D. C. of the solution and the solvent, respectively. For both salts D. C. remains nearly constant with increasing concentration below the critical micelle concentration, but increases considerably beyond that concentration.

D. C. of aqueous solutions of colloidal electrolytes involves many factors. (1) Sack[6] concluded that in an externally applied, field the electric fields of ions should hinder the orientation of water molecules, thus resulting in lower D. C. (2) According to the predictions of Debye-Falkenhagen's theory[7], the relaxation of ionic atmosphere should increase D. C. (3) If the solute molecules have dipole moments, such as ion-pairs[8], they will act to increase D. C., whereas (4) long hydrocarbon chains contained in the molecules will act to decrease it.

The volume fraction of the hydrocarbon chains is, however, only about 0.2 percent. at the concentration of 0.005 mole/l., assuming that their density is nearly the same as that of pure liquid paraffins, and according to Bruggeman's theory[9], the lowering of D. C. due to the hydrocarbon chains in this case is estimated to 0.3 percent,, so that we can consider this effect to be small at the range of concentration at which the measurement is carried out. Sack's effect should also be very small at the frequency of 2 Mc./sec. employed in this work, taking into account the results obtained with aqueous solutions of various electrolytes[10],[11]. The rise of D. C. beyond the critical micelle concentration shown in Fig. 1 may be due to Debye-Falkenhagen's effect or the orientation of dipoles

2) J. Wyman. *Phys. Rev.*, **35**, 623 (1930).
3) M. Shirai and B. Tamamushi, This Bulletin, **30**, 411 (1957).
4) M. Shirai and B. Tamamushi, *ibid.*, **29**, 733 (1956).
5) J. F. Johnson and R. H. Cole, *J. Am. Chem. Soc.*, **73**, 4536 (1951).
6) H. Sack, *Physik. Z.*, **27**, 206 (1926); **28**, 199 (1927).
7) P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928); *Z. Elektrochem.*, **34**, 562 (1928).
8) N. Bjerrum, *Erg. exakt. Naturwiss.*, **6**, 125 (1926).
9) D. A. G. Bruggeman, *Ann. d. Phys.*, **24**, 636 (1935).
10) F. H. Drake, G. W. Pierce and M. T. Dow, *Phys. Rev.*, **35**, 613 (1930).
1) R. T. Lattey and W. G. Davies, *Phil. Mag.*, **12**, 1111 (1931); **13**, 444 (1932).

TABLE II

DIELECTRIC CONSTANT AND EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF AMINE SALTS

substance	concn. (mole/l.)	ε (2 Mc./sec.)	Λ (1000c./sec.)
solvent: water	temp. 40°C		
hexadecylamine hydrochloride	0.0005	73.0	126
	0.0008	73.0	124
	0.001	73.0	123
	0.0012	73.0	111
	0.0015	73.0	92.0
	0.002	73.4	78.5
	0.003	73.9	60.6
	0.005	74.6	47.8
	0.01	75.2	35.4
octadecylamine hydrochloride	0.0001	73.0	118
	0.0002	73.0	117
	0.00025	73.4	112
	0.0003	73.8	106
	0.0005	74.8	79.8
	0.0008	75.3	50.9
	0.001	75.7	42.0
	0.002	76.7	31.5
	0.005	78.0	20.0
solvent: 2 mole/l. aq. ethanol		temp. 40°C.	
hexadecylamine hydrochloride	0.0005	70.5	82.2
	0.0008	70.5	81.0
	0.001	70.5	80.1
	0.0012	70.4	79.0
	0.0015	70.5	76.0
	0.002	70.7	70.3
	0.003	71.0	58.3
	0.005	71.2	48.0
	0.01	71.5	34.4
octadecylamine hydrochloride	0.0001	70.5	72.2
	0.0002	70.5	72.0
	0.00025	70.5	71.5
	0.0003	70.7	71.0
	0.0005	71.1	67.9
	0.0008	71.5	64.0
	0.001	71.7	61.0
	0.002	72.3	45.0
	0.005	72.9	24.0
solvent: 4 mole/l. aq. ethanol		temp. 40°C.	
hexadecylamine hydrochloride	0.0005	67.8	56.6
	0.0008	67.8	56.6
	0.001	67.8	57.2
	0.0012	67.8	58.0
	0.0015	67.8	59.0
	0.002	67.9	59.5
	0.003	67.9	59.7
	0.005	68.0	55.8
	0.01	—	45.7
octadecylamine hydrochloride	0.0001	67.8	47.5
	0.0002	67.8	47.5
	0.00025	67.8	47.0
	0.0003	67.8	47.0
	0.0005	67.8	46.6
	0.0008	67.8	47.5
	0.001	67.8	48.0
	0.002	68.0	50.6
	0.005	68.2	48.1

of ion-pairs, but below the critical micelle concentration the effect of both factors will become insignificant. The orientation of a micelle as a whole need not be considered, provided that the micelle is supposed to be in a liquid state of aggregation[1].

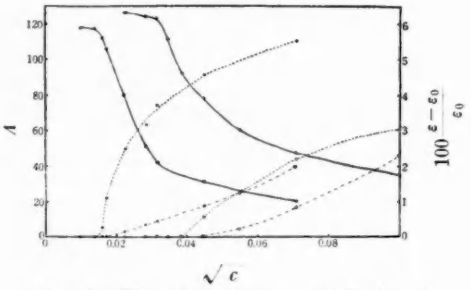

Fig. 1. The relative increase in D. C. and E. C. of amine salts in aqueous solution.
○, hexadecyl-;
●, octadecylamine hydrochloride.
equivalent conductivity at 700 c./sec.
the relative increase in D. C. at { 2 Mc./sec. / 30 Mc./sec.

3) **D. C. of solutions of salts in aqueous ethnol.**—D. C. and E. C. of solutions of hexadecyl- and octadecylamine hydrochloride in aqueous ethanol of 2 mole/l. and 4 mole/l. are shown in Table II as well as in Figs. 2 and 3. The rise of D. C. of these solutions beyond the critical micelle concentration is considerably reduced in the case of aqueous ethanol of 2 mole/l. and almost diminished in the case of aqueous ethanol of 4 mole/l. And, from the conductivity curves in Figs. 2 and 3, it is seen that the micelle formation is inhibited by the increase in alcoholic content of the solution of electrolytes. In aqueous ethanol solutions an anion and a cation of electrolytes tend to associate on account of the lower D. C. of the solvent medium, and therefore, the increase in D. C. due to the orientation of ion-pairs will become significant. On the other hand, in aqueous ethanol solutions the association of counter ions will be promoted and the micelle structure will become loose, and accordingly, Debye Frankenhagen's effect is expected to be reduced considerably.

4) **Effect of solubilization on D. C. of the solution.**—It is well known that water-insoluble substances, such as benzene, are dissolved in the interior of micelles, and

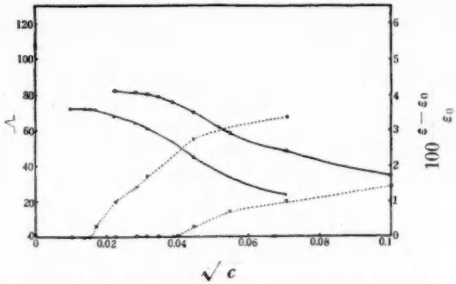

Fig. 2. The relative increase in D. C. and E. C. of hexadecyl- and octadecylamine hydrochloride in 2 mole/l. aq. ethanol.

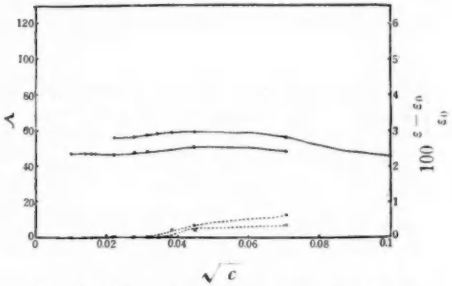

Fig. 3. The relative increase in D. C. and E. C of hexadecyl- and octadecylamine hydrochloride in 4 mole/l. aq. ethanol.

micelles are enlarged[12]. The larger the radius of the ions, the smaller the Debye-Falkengen's effect. Accordingly, when benzene is solubilized in solutions of colloidal electrolytes, D. C. of the solutions is expected to decrease. In Table III are indicated D. C. of aqueous solutions of octadecylamine hydrochloride containing various amounts of solubilized benzene. The result agrees with the above expectation.

TABLE III

DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF OCTADECYLAMINE HYDROCHLORIDE CONTAING VARIOUS AMOUNTS OF SOLUBILIZED BENZENE temp. 40°C

conc. of octadecylamine hydrochloride 0.003 mole/l.

moles of benzene per mole of amine salt	ε (2 Mc./sec.)
0	77.4
0.11	77.3
0.34	77.2
0.57	76.8
0.86	75.9
1.1	75.8

12) cf. A. E. Alexander and P. Johnson, "Colloid Science," Oxford Press (1949), p. 685.

5) **Dependence of D. C. on frequency.** —At the frequency of 2 Mc./sec., the relative increase of D. C. due to Debye-Falkenhagen's effect is significant, but at higher frequencies where the equivalent conductivity increases, the relative increase of D. C. should be diminished according to Debye-Falkenhagen's theory. In Table IV and Fig. 1 is shown the result of the measurement of D. C. of aqueous solutions of hexadecyl- and octadecylamine hydrochlorides at the frequency of 30 Mc./sec. At a certain concentration the relative increase of D. C. at 30 Mc./sec. is smaller than that at 2 Mc./sec., and this experimental fact agrees with our expectation, too. The ratio of D. C. at 30 Mc./sec. to that at 2 Mc./sec. becomes larger with increasing concentration. This is probably due to the shortening of the relaxation time of Debye-Falkenhagen's effect with increasing concentration.

TABLE IV

DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF AMINE SALTS AT 30 Mc./sec. temp. 40°C.

substance	conc. (mole/l.)	ε (30 Mc./sec.)
hexadecylamine hydrochloride	0.0005	73.0
	0.0008	73.0
	0.001	73.0
	0.0012	73.0
	0.0015	73.0
	0.002	73.0
	0.003	73.1
	0.005	73.6
	0.01	74.7
octadecylamine hydrochloride	0.0001	73.0
	0.0002	73.0
	0.00025	73.0
	0.0003	37.0
	0.0005	73.1
	0.0008	73.2
	0.001	73.3
	0.002	73.6
	0.005	74.4

From these exerimental results, it would be reasonable to conclude that the rise of D. C. observed in the case of aqueous solutions of long alkyl amine hydrochlorides is mainly due to Debye-Falkenhagen's effect. The same effect has been inferred from the result of measurement of high-frequency conductivity[1].

Summary

The dielectric constant and the equivalent conductivity of solutions of hexadecyl-

and octadecylamine hydrochloride have been measured at the frequencies of 2 Mc./sec. and 30 Mc./sec. The dielectric constant of the solutions shows a considerable increase beyond the concentration for micelle formation.

The dielectric constant and the equivalent conductivity of the solutions of these amine salts in aqueous ethanol of various concentrations have been measured. The rise of the dielectric constant is diminished with increasing concentration of ethanol.

The effect of solubilization of benzene on the dielectric constant of the solutions has been investigated. The relative increase in the dielectric constant is reduced with increasing amount of solubilized benzene.

From these experimental results, it is concluded that the rise of the dielectric constant of the aqueous solutions is mainly due to Debye-Falkenhagen's effect.

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Dielectric Investigation on Coals. II. Mixture of Coal Powder and Paraffin Wax.

By Keniti HIGASI, Isao MIYASITA and Yasutomo OZAWA

(Received March 17, 1957)

Introduction

Attempts have been described in a previous report[1] to prepare coal disks for examination from a coal block. Difficulties in the preparation of disks suitable for dielectric measurements are generally so great that this method can hardly be considered as practical or as convenient.

In the experiments described in the present article a new method using powdered coal was employed. The coal specimen is reduced to powder form, mixed with melted paraffin wax and cooled in a suitable mould. Test pieces prepared thus from the solidified materials contain usually 56 volume percent of coal. From the dielectric properties of these mixtures the dielectric constants and loss factors of the component coals are to be calculated by using a proper equation for mixtures.

Experimental

Six specimens of Japanese bituminous coal were examined. Five were chosen among those* studied in a previous paper: I Moziri No. 4, carbon, 85.25%; II Moziri No. 3, carbon, 81.71%; III Moziri No. 9, carbon, 82.98%; IIIa Moziri No.11, carbon, 82.07%; and Vc Mitui-Bibai No. 1-3, carbon, 80.62%. The remaining one is: B Mayazi North-No. 1, for which the proximate analysis is: moisture, 1.01; ash, 8.43; volatile matter, 41.04 and fixed carbon, 49.52%. Ultimate analysis for B is: ash, 2.47; C, 85.24; H, 5.86; O, 7.06; N, 1.67 and S, 0.16%. Paraffin wax used for preparing mixtures has the following properties at room temperature: dielectric constant, 2.46; loss factor, 0.0000 and specific gravity, 0.904.

Vitrain of coal specimen was pulverized in an agate mortar to a particle size below 100 meshes. The coal powder was dried in a desiccator at 105°C under 10^{-2} mmHg for 4-5 days. Then 15 g. of powder which had been thus thoroughly dried was poured into about 10 g. of melted paraffin wax, well mixed and solidified in a mould. A test piece of diameter ca. 40 mm and thickness ca. 5 mm was prepared from the solidified materials. Care was taken to secure uniform distribution of coal particles in the mixture.

The volume fraction of each mixture was controlled to have a constant value 0.56. Deviation from this standard was checked by collating the amounts of ash contained in the mixture and in the original coal specimen. Further examination was made of the range of errors in the final dielectric constant of coal which should arise from inaccuracies of the volume fraction taken (Fig. 1). Curve (b) represents the relation of Böttcher* between the dielectric constant of coal and that of mixture

1) I. Miyasita and K. Higasi, This Bulletin, **30**, 513 (1957).

* Chemical analyses of these samples were given in Ref. 1).

* See later reference.—Ref. 5).

TABLE I

DIELECTRIC CONSTANT (ε') AND LOSS FACTOR (ε'') OF COAL-POWDER PARAFFIN-WAX MIXTURE
(coal powder 56 vol%)

Sample No.		300c	1kc	3kc	10kc	100kc	300kc	1Mc	3Mc	10Mc	20Mc	50Mc
I	ε'	3.48	3.46	3.42	3.40	3.32	3.30	3.28	3.26	3.26	3.26	3.27
	ε''	0.0570	0.0492	0.0396	0.0365	0.0266	0.0287	0.0301	0.0259	0.0220	0.0213	0.0136
II	ε'	——	3.59	3.57	3.52	3.30	3.24	3.22	3.20	3.18	3.22	3.17
	ε''		0.0895	0.0805	0.0704	0.0270	0.0205	0.0183	0.0150	0.0147	0.0109	0.0159
III	ε'	3.40	3.38	3.34	3.32	3.26	3.22	3.21	3.21	3.19	3.18	3.18
	ε''	0.0295	0.0294	0.0268	0.0252	0.0212	0.0180	0.0185	0.0152	0.0129	0.0126	0.0114
IIIa	ε'	——	3.38	3.36	3.33	3.30	3.28	3.27	3.25	3.23	3.18	——
	ε''		0.0352	0.0295	0.0267	0.0222	0.0223	0.0206	0.0195	0.0186	0.00868	
Vc	ε'	3.61	3.57	——	3.51	3.46	——	3.42	——	3.37	——	——
	ε''	0.0600	0.0344		0.0327	0.0230		0.0247		0.0211		
B	ε'	3.34	3.33	——	3.32	3.28	——	3.26	——	3.24	——	——
	ε''	0.0390	0.0304		0.0256	0.0135		0.0139		0.0112		

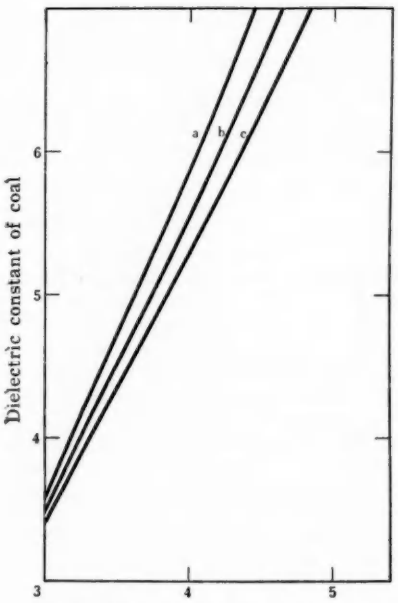

Fig. 1. The relation between the dielectric constant of coal itself and that of the powdered mixture as given by Böttcher equation. Volume fraction of coal in the mixture: curve a, 0.52; curve b, 0.56 and curve c, 0.60.

which has 56 vol% coal. If the volume percentages happen to become 52% or 60%—possibly they correspond to the maximum deviations—the relation between ε'_{coal} and $\varepsilon'_{mixture}$ will be represented by either curve (a) or (c). A glance at these curves will show that possible maximum error in ε'_{coal} amounts to several percent, viz., below $\pm 6\%$ for $\varepsilon'_{coal}<5$; below $\pm 6.4\%$ for $\varepsilon'_{coal}<6$.

Three methods of dielectric measurement were used in the frequency range covered. Measurements at frequencies from 300 c/s to 10 kc/s were carried out by means of an impedance bridge. Between 100 kc/s and 50 Mc/s a Q meter was used. A standing-wave method[2] of measuring dielectric properties was used at frequency of 4000 Mc/s.

The accuracy of measurement is considered, in general, to be $\pm$ 3 percent for ε'; but to be $\pm$ 15 percent at the microwave frequency. For ε'' the accuracy is much less, but the order of the values is reliable.

The results of measurements are collected in Tables I and II. They refer to paraffin-wax mixtures, having 56 vol% coal (Table I) and 50 vol% coal (Table II), respectively. All the measurements were carried out at room temperature.

TABLE II

DIELECTRIC CONSTANTS OF 50 VOL% MIXTURES OF MAYAZI COAL B OF VARIOUS DEGREES OF DRYING

condition	100 kc	300 kc	1Mc	3Mc	10 Mc	4000 Mc
vac. dry (v.d)	3.17	——	3.14	——	3.11	2.8
air dry (a.d)	3.36	——	3.34	——	3.30	2.8
wet (v.d-w)	3.75	3.64	3.54	3.51	3.30	3.0
wet (a.d-w)	4.62	4.44	4.31	4.18	4.03	2.7
paraffin*	2.43	——	2.40	——	2.37	2.32

* Paraffin wax employed in this measurement contained some impurities.

Discussion

There are available many equations[3,4] concerning the dielectric constants of non-homogeneous mixtures. Suppose that coal particles be nearly spherical in shape and that they be insulated by the medium

2) W. Jackson, *Trans. Faraday Soc.*, **42A**, 91 (1946).
3) W. F. Brown, *J. Chem. Phys.*, **23**, 1514 (1955); R. S. Smith, *J. Appl. Phys.*, **27**, 824 (1956).
4) M. Kubo and S. Nakamura, This Bulletin, **26**, 318 (1953); K. Higasi, *Monogr. Res. Inst. Appl. Elec.*, Hokkaido Univ., **5**, 9 (1955).

TABLE III

DIELECTRIC CONSTANTS OF COALS ESTIMATED BY USING THE FORMULAE OF BÖTTCHER (Bo) AND BRUGGEMAN (Br)

		300c	1kc	3kc	10kc	100kc	300kc	1Mc	10Mc	50Mc
I	Bo	4.45 (0.98)	4.41 (0.97)	4.33 (0.95)	4.29 (0.95)	4.12 (0.92)	4.08 (0.90)	4.04 (0.90)	4.00 (0.91)	4.02 (0.89)
	Br	4.49 (0.99)	4.44 (0.98)	4.35 (0.96)	4.32 (0.96)	4.14 (0.92)	4.10 (0.91)	4.05 (0.91)	4.00 (0.91)	4.02 (0.89)
II	Bo	—	4.68 (1.07)	4.64 (1.08)	4.53 (1.09)	4.08 (0.98)	3.96 (1.00)	3.92 (1.00)	3.84 (1.01)	3.81 (1.00)
	Br	—	4.71 (1.08)	4.68 (1.09)	4.56 (1.10)	4.10 (0.99)	3.97 (1.00)	3.94 (1.01)	3.84 (1.01)	3.82 (1.01)
III	Bo	4.29 (1.07)	4.25 (1.06)	4.17 (1.05)	4.12 (1.04)	4.00 (1.02)	3.92 (1.01)	3.90 (1.01)	3.86 (1.00)	3.84 (1.00)
	Br	4.32 (1.08)	4.27 (1.07)	4.18 (1.05)	4.14 (1.05)	4.00 (1.02)	3.94 (1.02)	3.91 (1.01)	3.86 (1.00)	3.84 (1.00)
IIIa	Bo	—	4.25 (1.01)	4.21 (1.02)	4.14 (1.01)	4.08 (1.02)	4.04 (1.04)	4.02 (1.04)	3.94 (1.04)	—
	Br	—	4.27 (1.02)	4.22 (1.02)	4.14 (1.01)	4.10 (1.03)	4.05 (1.04)	4.02 (1.04)	3.95 (1.05)	—
Vc	Bo	4.73 (1.00)	4.64 (0.99)	—	4.51 (1.01)	—	—	—	—	—
	Br	4.77 (1.01)	4.68 (1.00)	—	4.54 (1.01)	—	—	—	—	—

of paraffin wax. The following equation of Böttcher[5] is claimed to have general applicability to such a dispersed system

$$\frac{\varepsilon'-\varepsilon'_1}{3\varepsilon'} = v_2 \frac{\varepsilon'_2-\varepsilon'_1}{\varepsilon'_2+2\varepsilon'} \qquad (1)$$

in which ε', ε'_1 and ε'_2 are the dielectric constants* of the mixture, the paraffin wax and the coal particles, respectively, and v_2 is the volume fraction of the coal particle in the mixture.

Bruggeman's equation[6] which has been successfully applied to the analysis of rubber-carbon black mixtures[7] has the following form:

$$\frac{\varepsilon'_2-\varepsilon'}{\varepsilon'_2-\varepsilon'_1} = (1-v_2)\sqrt[3]{\frac{\varepsilon'}{\varepsilon'_1}} \qquad (2)$$

From the values of dielectric constants of mixtures recorded in Table I, the dielectric constants of the coals were calculated by using both Eqs. (1) and (2). The results of the calculation are shown in Table III in which Bo and Br denote Böttcher and Bruggeman, respectively. As the dielectric constants of these coal specimens are known by the direct determination on coal disks[1], a comparison between the estimated and actual values will be of interest. The ratio of $\varepsilon'_{\text{estimated}}/\varepsilon'_{\text{actual}}$ was taken for each sample and for each of the two equations—(See the values in parentheses in Table III). The general agreement may be regarded as satisfactory for most practical purposes.

In the above consideration it is assumed that the coal particles are insulated from each other by the paraffin-wax medium. On the contrary, coal particles are very densely packed in the mixture, so that in some places they must be touching each other. That is, some of them are supposed to be in good contact producing chains or larger aggregates. Considering this situation, two extreme cases will be examined for the sake of illustration. Suppose that neither coal particles nor paraffin wax are mixed but exist in a state of parallel layers. Let it be supposed in one case that the layers are parallel to the electric field; there will be the relation:

$$\varepsilon' = (1-v_2)\varepsilon'_1 + v_2\varepsilon'_2 \qquad (3)$$

and in the other case that they are all perpendicular to the field; there will be the relation:

$$\frac{1}{\varepsilon'} = \frac{1-v_2}{\varepsilon'_1} + \frac{v_2}{\varepsilon'_2} \qquad (4)$$

In order to make clear the relations existing among these equations of entirely different appearance, viz., Eqs. (1), (2), (3) and (4), an inspection of Fig. 2 will be useful in which on the basis of these equations ε'_2 is plotted against ε' using the same assumptions: $v_2=0.56$ and $\varepsilon'_1=2.46$. It is to be noted that curves 4 and 5 which represent Bruggeman and Böttcher equations, respectively, lie in the middle

5) C. J. F. Böttcher, *Rec. trav. chim.*, **64**, 47 (1945); C. J. F. Böttcher, "The Theory of Electric Polarisation," Elsevier, Amsterdam (1952), p. 417.

* Hereafter ε' and ε'_2 will be used instead of $\varepsilon'_{\text{mixture}}$ and $\varepsilon'_{\text{coal}}$, respectively.

6) D. A. G. Bruggeman, *Ann. Phys.*, **24**, 636 (1935).

7) B. Gross and R. M. Fuoss, *J. Phys. Chem.*, **60**, 474 (1956). See references cited there.

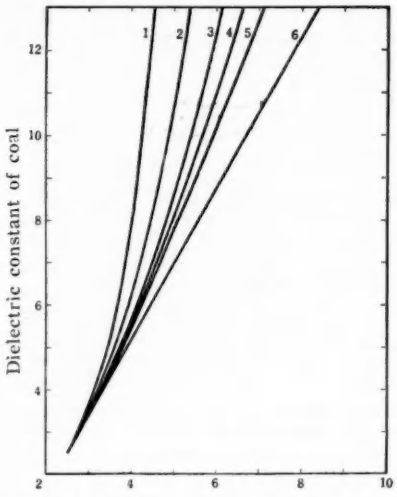

Fig. 2. Relations between the dielectric constant of coal itself and that of the powdered mixture with 56 vol % coal. Curve 1, given by Eq. (4) for a series arrangement; curve 2, Clausius-Mosotti relation; curve 3, Eq. (6) of Lewin; curve 4, Eq. (2) of Bruggeman; curve 5, Eq. (1) of Böttcher; and curve 6, Eq. (3) for a parallel arrangement.

part of the region outlined by curves 1 and 6 which are given by Eqs. (4) and (3).

As the mixture in the present study is not to be considered as a homogeneous phase, the use of the Clausius-Mosotti equation to which Groenewege et al.[8] referred, will be absurd. But as is seen by curve 2 in Fig. 2 this equation does represent some average state between those defined by Eqs. (4) and (1) or Eqs. (4) and (2).

Next, let the case be examined when the coal component has a different volume fraction from 0.56. In Table IV the case of 50 vol % coal is studied. Estimated values from 50 % are in good agreement with those from 56 %. Consequently, it may be concluded that the use of Eqs. (1) and (2) is justified so far.

TABLE IV

ESTIMATED DIELECTRIC CONSTANTS FOR MAYAZI COAL (vac. dry)

		100kc	1Mc	10Mc	4000Mc
Bo	56%	4.04	4.00	3.96	——
	50%	4.05	4.02	3.99	3.34
Br	56%	4.05	4.00	3.97	——
	50%	4.08	4.04	4.00	3.35

8) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

It is to be noted that the above equations are related only to the dielectric constant and not to the loss factor. A more general equation including the latter has recently been provided by Lewin[9] for the case of perfectly spherical particles* in insulating medium. For the complex dielectric constants as defined by $\varepsilon^*=\varepsilon'-j\varepsilon''$, $\varepsilon_1^*=\varepsilon_1'-j\varepsilon_1''$ and $\varepsilon_2^*=\varepsilon_2'-j\varepsilon_2''$, the following equation holds:

$$\varepsilon^*=\varepsilon_1^*\left(1+\frac{3v_2}{\dfrac{\varepsilon_2^*F(\Theta)+2\varepsilon_1^*}{\varepsilon_2^*F(\Theta)-\varepsilon_1^*}-v_2}\right), \qquad (6)$$

where

$$F(\Theta)=\frac{2(\tan\Theta-\Theta)}{(\Theta^2-1)\tan\Theta+\Theta},$$

and

$$\Theta=\frac{2\pi a}{\chi}\sqrt{\varepsilon_2^*}$$

in which a is the radius of the coal particle and λ is the wave length of the electric wave used in the dielectric measurement. The application of Eq. (6) to the present problem was made first for the case when there is no loss factor (see curve 3 in Fig. 2). Then calculation was repeated for the cases when the mixtures have appreciable loss factors. It was ascertained by these calculations that even when ε'' amounts to a considerable magnitude 0.1**, the dielectric constant can be safely estimated within experimental error with the payment of little attention to the presence of the loss factor.

Böttcher and Bruggeman equations have been originally derived only for real dielectric constants, but they may be transformed into more general equations including the imaginary part when a complex dielectric constant is used instead of the real one. It can be proved by numerical calculations using the general equation of Böttcher thus obtained that the existence of appreciable loss factors does not vitiate the results of the estimation shown in Table III.

9) L. Lewin, *J. Inst. Elec. Engrs.*, **94**, 65 (1947); E. Meyer, H. J. Schmidt und H. Severin, *Z. angew. Phys.*, **8**, 257 (1956).

* A comparison of the theoretical curve 3 (Fig. 2) for perfectly spherical particles with the experimental data will suggest that the formation of chains does occur in the mixture.

** The maximum value of ε'' observed in the present study is 0.0895 at 1 kc/s obtained for the coal sample II.

Lastly the results shown in Table II will be again considered. It will be seen that an air-dry sample—coal powder was dried in air for 4–6 days at 105°C—has a slightly higher dielectric contant than that of the vacuum dried sample. This may indicate that some polar substances are produced upon oxidation*. Further, water absorption by dried samples (air-dry as well vac-dry samples) greatly increases the dielectric constant.

It should be noted that all the samples come to have the same dielectric constant of about 2.8 at the frequency of 4000 Mc/s. This fact suggests that all the dipoles in the coal—irrespective of whether they originally belong to the coal, or are produced on oxidation, or are of the water molecules adsorbed by the coal—are completely blocked from rotation**. Further this view is substantiated by the fact that the dielectric constant 3.35 for coal at this frequency of 4000 Mc/s can be regarded as the optical dielectric constant (See Table IV). In fact this magnitude is just equal to the square of the refractive index[10] of the coal having the same carbon content.

* See, in this connection, W. N. Adams and G. J. Pitt, *Fuel*, **34**. 383 (1955).

** The condition of non-rotation of dipoles is not satisfied in the liquid state until the frequency become higher than 30,000 Mc/s (at room temperature). The corresponding frequency in the solid state is expected to be low, since the viscosity or the hindering potential of rotation should be much higher than in the liquid state (C. P. Smyth, "Dielectric Structure and Behavior," (1955)).

10) D. W. van Krevelen, *Brennstoff-Chem.*, **34**, 167 (1953).

Summary

A new method using powdered coal and paraffin wax was proposed for measuring the dielectric constant of coal concerned. In order to check the validity of this method, experiments were conducted on five coal specimens for which direct determination of dielectric constant had been made by the writers. Special attention was paid to the choice of a mixture formula and also to the influence of the electric conductivity upon the dielectric constant. It was concluded then that the present method could reproduce the dielectric constant of the coal with the fair precision of ± 10%.

The microwave measurement on one specimen reveals that all the dipoles in coal are completely inhibited from rotation at this frequency.

The writers wish to thank Prof. G. Takeya, Faculty of Engineering, for supplying the coal samples examined in this paper.

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Dielectric Investigation on Coals. III. On a Variety of Coals

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Introduction

A preceding paper[1] has shown that by a method using mixture of powdered coal and paraffin wax, the dielectric constant of coal could be estimated with fair precision of ±10 per cent. It has been pointed out that almost the same amount of deviation is to be found when testing different samples of the same specimen.

The present article deals with the dielectric constant data obtained by using the mixture method on a variety of Japanese coals and on five coals from foreign sources.

1) K. Higasi, I. Miyasita and Y Ozawa, This Bulletin, **30**, 546 (1957).

Experimental

Coal samples here examined do not include all the types of Japanese coals, but are representative caking coals produced in Japan. Some of the conclusions reached for them will be applicable to all other Japanese coals. Foreign coals are chosen from among those which have been imported to certain iron works in Japan. Chemical analyses of all these coal specimens are recorded in Tables I and II.

The coal samples were reduced to fine powders, thoroughly dried at 105°C in a vacuum, and then mixed with melted paraffin wax[1]. The volume

TABLE I

PROXIMATE ANALYSES

Coal No.	Source of Sample	Moisture	Ash	Volatile matter	Fixed carbon	Total sulfur
A1	Yubari No. 2—10	1.38	4.71	51.44	42.47	—
B1	Mayazi No. 1a	0.97	1.80	43.38	53.85	—
B2	Mayazi No. 2	0.72	1.61	47.37	50.30	—
B3	Mayazi No. 3	1.11	2.26	47.29	49.34	—
C1	Sunagawa No. 2	1.02	4.35	44.63	50.00	—
C2	Sunagawa No. 3	0.83	6.85	38.67	53.65	—
C3	Sunagawa No. 4	2.65	4.68	48.65	44.02	—
C4	Sunagawa No. 8	1.20	2.54	46.26	50.00	—
C5	Sunagawa No. 9	2.30	3.61	57.06	37.03	—
C6	Sunagawa No. 10	1.78	8.93	52.76	36.53	—
C7	Sunagawa No. 11	1.13	6.36	42.83	49.68	—
D1	Yatake	1.11	2.94	21.29	74.86	0.65
E1	Taihei (lignite)	12.86	5.84	45.33	35.97	0.76
E2	Tempoku (brown coal)	12.80	1.52	35.62	50.06	0.77
F1	India	—	14.96	27.65	57.39	—
F2	Pocahontas, Western (U. S. A.)	—	7.33	22.00	70.67	—
F3	Pocahontas (U. S. A.)	—	5.92	18.60	75.48	—
F4	Pocahontas (U. S. A.)	—	4.85	19.30	75.85	—
F5	Durham (England)	0.85	1.70	26.14	71.31	—

TABLE II

ULTIMATE ANALYSES (dry, ash-free basis)

Coal No.	Source	C%	H%	O%	N%	S%
C3	Sunagawa No. 4	82.09	6.21	10.26	1.36	0.09
C7	Sunagawa No. 11	81.84	5.50	10.75	1.59	0.32
D1	Yatake	89.4	4.86	3.06	1.88	0.64
E1	Taihei	65.1	4.93	28.42	0.93	0.62
E2	Tempoku	70.2	4.74	23.4*	1.10	0.6
F1	India	88.03	5.28	4.69	1.66	0.34
F4	Pocahontas	87.99	4.98	5.17	1.51	0.35
F5	Durham (England)	89.31	4.31	—	—	—

* Estimated from (O+S)% 23.96 on the assumption S% 0.6.

fraction of the coal was kept as 0.56 of the whole part.

The dielectric measurements[2] were made at room temperature with a Q meter for the frequency range of 50 Mc/s to 100 kc/s, and with an impedance bridge for the range of 10 kc/s to 300 c/s.

The results of measurements are collected in Tables III and IV. Dielectric constants, ε' and loss factors, ε'' without parenthesis all refer to the paraffin-wax mixtures of 56 vol % coal. Figures in parentheses show the dielectric constants of the coals themselves which were obtained by the use of the following mixture formula due to Böttcher[3].

$$\frac{\varepsilon'-\varepsilon'_1}{3\varepsilon'} = v_2 \frac{\varepsilon'_2-\varepsilon'_1}{\varepsilon'_2+2\varepsilon'} \qquad (1)$$

in which ε', ε'_1, and ε'_2 are the dielectric constants of the mixture, the paraffin wax and the coal particles, respectively, and v_2 is the volume fraction of the coal particles in the mixture.

When the mixture has an appreciable loss factor, the application of Eq. (1) becomes questionable. For instance, the mixture with the British sample (F5) has ε'' 0.284 at the frequency of 1 kc/s. To check errors arising from this, a general equation for complex dielectric constant $\varepsilon^*=\varepsilon'-j\varepsilon''$ derived from Eq. (1) was employed for comparsion's sake. By putting $\varepsilon^*=4.79-0.284j$ in this modified equation, the following values of the coal were obtained: $\varepsilon_2^*=7.36-0.664j$ in contrast to $\varepsilon_2'=7.37$ obtained from Eq. (1) (See Table IV). This one example will illustrate well the validity of other approximate calculations on Eq. (1).

As the error due to conductivity is very important, a further check was made by the use of an equation presented by Lewin[4]. The results were: $\varepsilon^*=4.79-0.284j$ gives $\varepsilon_2^*=7.96-0.895j$

2) I. Miyasita and K. Higasi, This Bulletin, **30**, 513 (1957).

3) C. J. F. Böttcher, *Rec. trav. chim.*, **64**, 47 (1945); and cf. ref. 1) above.

4) L. Lewin, *J. Inst. Elec. Engrs.*, **94**, 65 (1947).

TABLE III

DIELECTRIC CONSTANTS (ε') AND LOSS FACTORS (ε'') OF JAPANESE COALS*

(Paraffin-wax mixture, coal 56 vol %)

Coal No.		300 c	1 kc	10 kc	100 kc	1 Mc	10 Mc
A1	ε'	3.36 (4.21)	3.32 (4.12)	3.30 (4.08)	3.27 (4.02)	3.24 (3.96)	3.24 (3.96)
	ε''	0.0333	0.0212	0.0144	0.0087	0.0115	0.0083
B1	ε'	3.24 (3.96)	3.24 (3.96)	3.24 (3.96)	3.22 (3.92)	3.19 (3.86)	3.16 (3.79)
	ε''	0.0256	0.0193	0.0135	0.0088	0.0080	0.0068
B2	ε'	3.29 (4.06)	3.28 (4.04)	3.26 (4.00)	3.25 (3.98)	3.22 (3.92)	3.22 (3.92)
	ε''	0.026	0.0198	0.0154	0.0109	0.0082	0.0080
B3	ε'	3.28 (4.07)	3.24 (3.96)	3.24 (3.96)	3.22 (3.92)	3.19 (3.86)	3.15 (3.77)
	ε''	0.0242	0.0176	0.0145	0.0113	0.0097	0.0085
C1	ε'	3.39 (4.27)	3.36 (4.21)	3.36 (4.21)	3.31 (4.10)	3.30 (4.08)	3.30 (4.08)
	ε''	0.0309	0.0252	0.0170	0.0089	0.0131	0.0112
C2	ε'	3.29 (4.06)	3.28 (4.04)	3.24 (3.96)	3.22 (3.92)	3.18 (3.84)	3.17 (3.81)
	ε''	0.0312	0.022	0.019	0.0135	0.0100	0.0065
C3	ε'	3.11 (3.69)	3.08 (3.63)	3.06 (3.59)	3.05 (3.58)	3.04 (3.56)	3.02 (3.52)
	ε''	0.0180	0.0135	0.0103	0.0097	0.0072	0.0059
C4	ε'	3.34 (4.17)	3.32 (4.12)	3.28 (4.04)	3.26 (4.00)	3.24 (3.96)	3.24 (3.96)
	ε''	0.0242	0.0161	0.0147	0.0114	0.0096	0.0095
C5	ε'	3.42 (4.33)	3.34 (4.17)	3.32 (4.12)	3.21 (3.90)	3.19 (3.86)	3.17 (3.82)
	ε''	0.0570	0.0407	0.0290	0.0153	0.0154	0.0128
C6	ε'	3.44 (4.37)	3.40 (4.29)	3.37 (4.23)	3.37 (4.23)	3.32 (4.12)	3.31 (4.10)
	ε''	0.0320	0.0190	0.0132	0.0099	0.0086	0.0099
C7	ε'	3.36 (4.21)	3.34 (4.17)	3.29 (4.06)	3.28 (4.04)	3.25 (3.98)	3.22 (3.92)
	ε''	0.0407	0.0272	0.0168	0.0080	0.0097	0.0098
D1	ε'	3.08 (3.55)	3.07 (3·53)	3.02 (3.43)	3.01 (3.41)	3.03 (3.45)	3.00 (3.40)
	ε''	0.034	0.0248	0.0126	0.0097	0.0053	0.00306
E1	ε'	3.76 (4.83)	3.73 (4.78)	3.61 (4.56)	3.59 (4.52)	3.55 (4.45)	3.44 (4.24)
	ε''	0.115	0.0904	0.0482	0.0421	0.043	0.0428
E2	ε'	3.64 (4.61)	3.62 (4.58)	3.57 (4.48)	3.58 (4.50)	3.52 (4.38)	3.46 (4.27)
	ε''	0.031	0.0284	0.023	0.0248	0.0256	0.0312

* Values in parenthesis refer to ε' of coals themselves.

while $\varepsilon^*=4.79-0.00j$ gives $\varepsilon_2^*=7.99-0.00j$. Again there is hardly any significant difference between the values of ε'_2, i. e. 7.96 versus 7.99.

A comparison of the values of Tables III and IV would reveal that the coals from foreign sources here examined exhibit entirely different dielectric behavior from the Japanese coals. In all of them strong frequency dependence of dielectric properties is found which is not so pronounced in most of the Japanese specimens.

The ε' values of Japanese coals generally show slight increases at the lower frequency side. Among them two samples E1 and E2 of higher oxgen contents may be noted, since they have a little higher value in ε' and show somewhat noteworthy dependence of ε'' upon frequency.

TABLE IV

DIELECTRIC CONSTANTS (ε') AND LOSS FACTORS (ε'') OF COALS* FROM FOREIGN SOURCES
(Paraffin-wax mixture, coal 56 vol %)

Ccal No.		300 c	1 kc	10 kc	100 kc	1 Mc	10 Mc
F1	ε'	4.93 (7.69)	4.62 (6.98)	4.12 (5.84)	3.91 (5.37)	3.74 (5.00)	3.60 (4.71)
	ε''	0.53	0.419	0.285	0.149	0.097	0.0588
F2	ε'	4.62 (6.98)	4.43 (6.53)	4.11 (5.81)	4.04 (5.66)	3.82 (5.18)	3.68 (4.87)
	ε''	0.315	0.236	0.187	0.115	0.0867	0.0760
F3	ε'	4.66 (7.07)	4.41 (6.48)	4.14 (5.88)	3.96 (5.48)	3.82 (5.18)	3.66 (4.83)
	ε''	0.318	0.246	0.151	0.116	0.0902	0.0688
F4	ε'	4.66 (7.07)	4.48 (6.64)	4.14 (5.88)	3.97 (5.51)	3.81 (5.16)	3.66 (4.83)
	ε''	0.359	0.262	0.171	0.123	0.0948	0.0768
F5	ε'	5.01 (7.88)	4.79 (7.37)	4.44 (6.55)	4.22 (6.06)	3.97 (5.51)	3.82 (5.18)
	ε''	0.327 [0.775]	0.284 [0.664]	0.196 [0.448]	0.143 [0.321]	0.120 [0.264]	0.0936 [0.203]

* Values in parenthesis are ε' of coals and those in square bracket refer to ε'' of the coal concerned.

The behavior of ε'' of E1 and E2 is entirely different from other Japanese coals. Definite increase in ε'' with increasing frequency is found in these samples as was found in Tempoku brown coal[2], indicating the existence of some dispersion which is probably due to the rotation of OH groups.

As a general trend there is observed a slight increase of ε'' at the lower frequency side in most of the Japanese coals. No definite explanation can be offered for this phenomenon. Possibly it may be due to the presence of impurities such as trace of water which forms a conducting phase*.

Discussion

Having obtained rather ample data of dielectric constants of coals, either directly determined in a previous study[2] or indirectly estimated in the present research, it was thought of interest to make some comparison between the dielectric constant and other properties of coal.

To begin with, the change of the dielectric constant with carbon-content (dry, ash-free) will be examined. As the observed dielectric properties are not independent of the frequency of the measurement**, two graphs of ε' vs. C % plots are drawn for two representative frequencies, 1 kc/s and 1 Mc/s (Figs. 1 and 2).

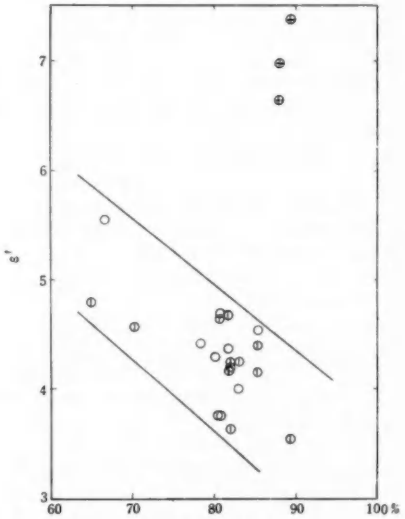

Fig. 1. Dielectric constants measured at frequency of 1 kc/s of coals of various carbon contents. ○, determined directly on Japanese coals; ①, estimated from powdered mixtures on Japanese coals; ⊕, ditto on foreign coals.

Among the widely scattered points there appears to be a general trend of increase in dielectric constant with decrease in carbon-content.

According to the infra-red absorption

* See for instance, C. P. Smyth, "Dielectric Bahavior and Structure," McGraw-Hill Book Co., New York (1955), p. 191.

** The curves in Fig. 3 illustrate different types of dependence of the dielectric constant upon the frequency.

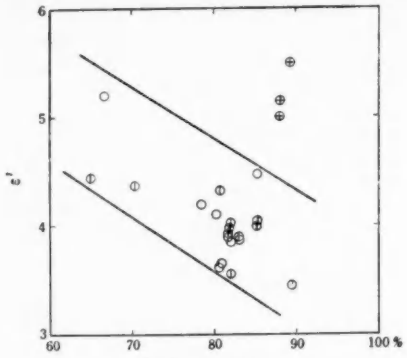

Fig. 2. Dielectric constants measured at frequency of 1 Mc/s of coals of various carbon contents. ○, ⓘ and ⊕, the same with Fig. 1.

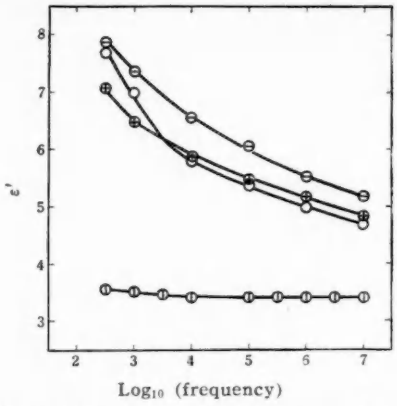

Fig. 3. Dielectric constant-frequency curves of high rank coals. ⓘ, Yatake (Japan); ○, Indian coal; ⊕, Pocahontas (U. S. A.); ⊖, Durham (U. K.).

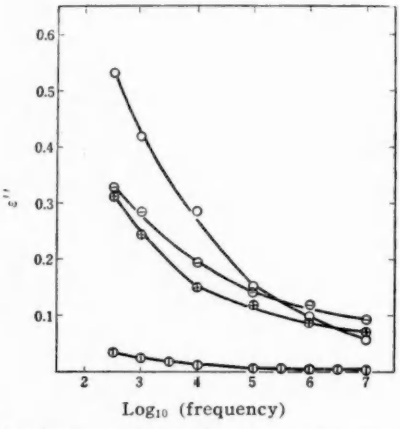

Fig. 4. Loss factor-frequency curves of powdered mixtures of high rank coals. ⓘ, ○, ⊕ and ⊖, the same with Fig. 3.

studies[5,6] the intensities of bands concerning oxygen-containing groups of coal constituents, especially of the bonded OH at near 3.3 μ, appear to decrease as the oxygen-content decreases. These intensities become greater in the low rank coals of which the carbon-contents are in the range from 78 to 84 per cent. They fall in the higher rank coals, especially over 89 per cent carbon coals.

The oxygen-containing groups which appear to be rich in the low rank coals are provided with large electric moments. If the rotation of these polar groups is possible to a certain extent, they would make effective contributions to the dielectric constant.

Consequently it would be reasonable to conclude that the lower rank coals have the higher dielectric constants on account of the higher content of polar groups such as OH or CO.

In the range of carbon 88 to 90 per cent, very remarkable differences are recognized between the dielectric constants of foreign coals and of the Japanese coal here examined (See Fig. 1). The change in ε' of these coals with frequency is shown in Fig. 3. The value of Yatake coal (C % 89.4) is low and almost independent of frequency, while others (F1, F4 and F5) show pronounced anomalous dispersion: the dielectric constants greatly decrease with increasing frequency.

Regarding the foreign coals it will be of interest to examine the relation between the loss factor and frequency. In Fig. 4 ε'' values of the mixtures of coal and paraffin wax are shown. In each of them a steep rise of ε'' value is found in the lower frequency region. This also makes a remarkable contrast to the almost flat curve of Yatake coal.

Non-dispersive character is not limited to Yatake coal. Most of the Japanese bituminous coals (C % 80–87) may be regarded as lacking in anomalous dispersion*

5) J. K. Brown, *J. Chem. Soc.*, 744 (1955).
6) R. A. Friedel and J. A. Queiser, *Anal. Chem.*, **28**, 22 (1956).

* There is found an increase in ε'' values at the low frequency side, but as compared with values of coals from foreign sources the magnitude of this increase is small so that possibly it may be attributed to the presence of impurities.

(See the results for A1, B1-3, C1-4, C6-7 and D1 in Table III and data of previous reports[1,2]). Their dielectric constants are generally low — their dielectric properties in general resemble those of ordinary electric insulators.

It may be worth while to cite the results of infrared absorption studies on Japanese coals recently reported by Kozima and his co-workers[7]. The ratio of C_{arom}—H to C_{aliph}—H on the same specimens of Japanese coals, A1 and D1, of the present study was determined by them*. It was pointed out then that the ratio of Yatake coal (C % 89.4) was four times larger than that of Yubari coal (C % ca. 85.5). This remarkable difference, however, is not reflected in the dielectric constant (See Table III).

According to the above facts the following views would be offered. They are not merely of presumptive evidence based only upon the present results.

1) The high ε' values of foreign coals are due to the condensed aromatic structures with pi-electrons[8]. As described by van Krevelen and his co-workers[9] the influence of electric conductivity is evident. The loss factor-frequency curves in Fig. 4 are of the shape to be expected for a system of semi-conductor particles densely packed in an insulating medium[10,11].

2) Japanese high-rank bituminous coals as represented by Yatake coal appear to have rather different structures from the foreign coals. They are relatively poor in condensed aromatic structures. Possibly they are rich in hydroaromatic rings or in alkyl side chains[12].

Summary

By using a method of paraffin-wax mixture dielectric constants were determined for a variety of coals including five specimens from foreign sources. It was found that dielectric constants of lower rank coals are generally higher than those of bituminous coals of higher rank. Large difference in dielectric behavior was detected among the coal specimens (C % 87–90) from different sources. The present dielectric measurement supported the view that the nature of Japanese coals is particular as compared with European and American coals.

The writers wish to thank Professor G. Takeya for his kind interest and also for supplying the coal samples examined in this paper. Cordial thanks are also due to Dr. Y. Ozawa and to Mr. Y. Zyomoto for their friendly help in this work.

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7) K. Kozima, K. Sakasita and T. Yosino, *J. Chem. Soc. Japan* (Pure Chem.) **77**, 1432 (1956)

* These coal specimens were kindly provided by Dr. H. Honda, Resources Research Institute, Kawaguti-City, both to Prof. Kozima and to one of the present writers.

8) H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 28 (1952).

9) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

10) C. P. Smyth, op. cit. p., 191.

11) B. V. Hamon, *Austra. J. Phys.*, **6**, 304 (1953).

12) A. Baba, "Progress in Coal Science," Vol. 2, Hakuasyobo. Tokyo (1956), p. 86.

Dielectric Investigation on Coals. IV. Notes on Dipole Moment

By Keniti HIGASI, Yosie HIGASI and Isao MIYASITA

(Received March 17, 1957)

Introduction

Some years ago it was suggested to one of the present writers that a determination of electric dipole moment should be most desirable for coals. Indeed, the usefulness of dipole moments for attacking problems in structural chemistry has long been appreciated[1]. As was true in the cases of simpler molecules, it was then hoped, they migt become the most effective means among the various physical methods applicable for the study of coal structure.

Now, rather ample data[2,3] on the dielectric properties of coals being available, it was thought worth while to make some trials in this direction. One may say that such a trial is destined to be labour lost, since in the solid state the orientation of polar groups is almost completely restricted by lattice forces. However, coals differ from most of the crystalline solids. According to van Krevelen[4] the main constituent such as vitrain is to be regarded as a supercooled liquid. Perhaps coals are sorts of organic glasses or polymers[4]. If this view be correct, one may use equations for liquids in determining a dipole moment[5]. This affords a basis for the trial and speculations to be described in the present paper.

Equations of Liquids

From among many equations for liquids, the Onsager equation[6] is the only one to have been used extensively in calculating the dipole moment.

$$\mu^2 = \frac{9kT}{4\pi N}\,\frac{M}{d}\,\frac{(2\varepsilon+\varepsilon_\infty)(\varepsilon+2)}{3\varepsilon(\varepsilon_\infty+2)} \times\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right) \qquad (1)$$

in which μ is the molecular dipole moment, k is the Boltzmann constant, T is the absolute temperature, N is the Avogadro number, M is the molecular weight and d is the density. In the above equation ε is the ordinary dielectric constant*, while ε_∞ is the optical dielectric constant, or the dielectric constant measured at the frequencies which are so high that the permanent dipoles are unable to exert any influence. In the original form of Eq. (1) the square of refractive index, n^2 is used instead of ε_∞. The above equation is a modification due to Smyth[7] and useful for the present work, where the atom polarization may play a significant role.

The Debye equation is originally an equation for gases and vapours. Its use will be considered on account of the simpler form:

$$\mu^2 = \frac{9kT}{4\pi N}\,\frac{M}{d}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right) \qquad (2)$$

The Onsager equation holds mostly for highly polar liquids[8,9]. On the contrary the Debye equation is known to be valid for non-polar liquids and a few groups of polar liquids such as ethers[10], amines[11] and chloroform[12]. There is uncertainty as to the choice of a proper equation for liquids, if other equations excepting the above two are left out of consideration.

The difference in the above equations lies in the factor

$$S = \frac{(2\varepsilon+\varepsilon_\infty)(\varepsilon+2)}{3\varepsilon(\varepsilon_\infty+2)} \qquad (3)$$

1) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York (1955); J. W. Smith, "Electric Dipole Moments," Butterworths Sci. Publ., London (1935). K. Higasi, "Foundation of Structural Chemistry—Dipole Moments," Kawade Book Co., Tokyo (1952).
2) I. Miyasita and K. Higasi, This Bulletin, **30**, 513 (1957).
3) I. Miyasita, K. Higasi and M. Kugo, This Bulletin, **30**, 550 (1957).
4) D. W. van Krevelen, *Brennstoff-Chem.*, **34**, 167 (1953).
5) C. P. Smyth, *op. cit.*, p. 226; J. W. Smith, *op. cit.*, p. 145; K. Higasi, *op. cit.*, p. 14.
6) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

* In the present article ε will be used instead of ε'.
7) C. P. Smyth, *op. cit.*, p. 23.
8) C. J. F. Böttcher, *Physica*, **6**, 59 (1939).
9) H. Fröhlich, *Trans. Faraday soc.*, **42A**, 39 (1946).
10) K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **24**, 57 (1934).
11) M. Shirai, This Bulletin, **29**, 518 (1956).
12) R. J. W. Le Fèvre et al., *J. Chem. Soc.*, 487, 491, 496 (1936).

If $S=1$*, Eq. (1) will become the same with Eq. (2).

In most bituminous coals both values of ε and ε_∞ (as estimated from n) do not much vary with the specimen. On putting some average values, $\varepsilon=4$ and $\varepsilon_\infty=3.24$, in Eq. (3), S will be evaluated as 1.07. Consequently the dipole moment calculated from Eq. (1) slightly differs from that estimated by Eq. (2), the difference being only 3–4 per cent. This result is very encouraging, since an error of less than 5% in moment is insignificant in the present case.

Both Eqs. (1) and (2) can be reduced to a very simple equation

$$\mu=A[(\varepsilon-\varepsilon_\infty)M/d]^{1/2} \quad (4)$$

where A has the values

$$A_1^2=0.147/(\varepsilon+2)(\varepsilon_\infty+2) \quad \text{(Debye)} \quad (5)$$

$$A_2^2=0.147(2\varepsilon+\varepsilon_\infty)/3\varepsilon(\varepsilon_\infty+2)^2 \quad \text{(Onsager)} \quad (6)$$

in which dipole moment μ is expressed in Debye unit (10^{-18}e.s.u.cm.) and the temperature is assumed to be 20°C.

Further, in a rough estimation the coefficient A may be regarded as a constant. Usually for coals of C% 65–90 ε lies between 3.3–5.5 and ε_∞ between 2.8–4.0 (see Tables I and II). The values of A (Debye) are 0.075–0.057 and A (Onsager) 0.078–0.061, respectively.

For $A=0.068$ ($\varepsilon=4$, $\varepsilon_\infty=3.24$) and $M/d=300$ cc Eq. (4) becomes

$$\mu=1.17\sqrt{\varepsilon-\varepsilon_\infty} \quad (7)$$

The above equation is incorrect but convenient for a quick judgement. Moment values calculated from Eq. (7) are shown by curve b in Fig. 1. In this figure two other curves a and c are drawn for the cases with $M/d=400$ and 200, respectively.

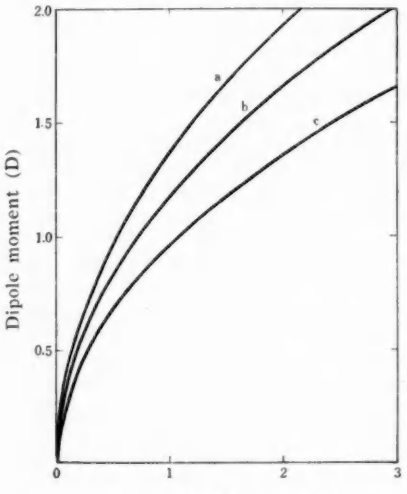

Fig. 1. Dipole moment of coal as a function of the quantity $\varepsilon-\varepsilon_\infty$. Curve a, $M/d=400$; curve b, $M/d=300$; and curve c, $M/d=200$.

* If ε is equal to ε_∞, S will become unity. See further Böttcher, "The Theory of Electric Polarisation." Elsevier Publ. Co., Amsterdam (1952).

Dielectric Constant

Both Eqs. (4) and (7) well illustrate the physical significance of the dielectric constant. The dielectric constant ε of a polar substance has three origins: (a) the orientation effect of the permanent dipole, (b) the displacement effect of the atoms, and (c) the displacement effect of the electrons. As the optical dielectric constant ε_∞ is contributed only from the latter two effects, the difference $\varepsilon-\varepsilon_\infty$ represents the part of dipole orientation.

As the dielectric constant is a function of frequency, a question arises as to the method of choosing a proper ε value for the calculation. In the study of liquids, ε values at frequencies 1–10 Mc/s have been usually employed[13], because the measurement is easiest at these frequencies and also because the obtained values are generally equal to static dielectric constants. As the relaxation time is expected to be different from liquids, a more cautious attitude is demanded in treating coals. Before being able to choose a proper value of ε one must examine the dependence of the dielectric constant upon frequency.

There are found in coals at least three types of frequency dependences. In one of them (A type) there is apparently little dispersion: that is, both the dielectric constant and loss factor have values almost indepedent of frequency in the range of 300 c/s—50 Mc/s. See curves (A) in Figs. 2 and 3. Examples: most of the Japanese bituminous coals. In the second type (B type), dispersion appears to exist in the high frequency region. Examples: Tempoku brown coal (specimen VI) and probably two other low rank coals (E1 and E2). The third type (C type) is charac-

13) C. P. Smyth, *op. cit.*, p. 209; J. W. Smith, *op. cit.*, p. 30; Y. Morino and I. Miyagawa, *Kagaku-no-Ryoiki*, Spec. no., **8**, 1 (1953).

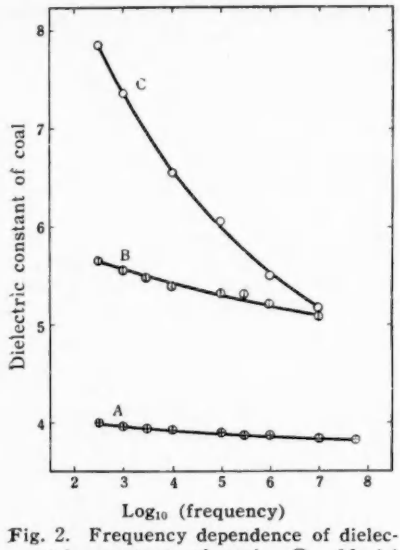

Fig. 2. Frequency dependence of dielectric constant of coal. ⊕, Moziri bituminous coal; ①, Tempoku brown coal; and ○, British coal (Durham). Data for the British coal were obtained from powdered mixture.

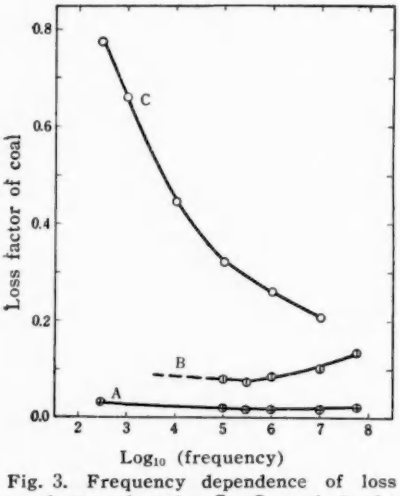

Fig. 3. Frequency dependence of loss factor of coal. ⊕, ①, and ○, the same with Fig. 2.

terized by high loss factor and high dielectric constant at the low frequency region. Examples: European and American high rank coals (F1–5).

In view of the above facts the following assumptions will be taken as a basis for some considerations.

1) For A type coals, 1 Mc/s values are preferred. The Q meter gives most reliable values when measured at this frequency.

2) For B type coals, 1 kc/s values are taken. Lower frequency values in general may be preferable. But there is no guarantee that moisture was completely removed. The impedance bridge gives best values at 1 kc/s.

3) For C type coals, 10 Mc/s values are arbitrarily selected. It is questionable whether the dipole rotation at this high frequency is as free as at the static fields. But the high ε values at low frequencies may not be attributable to the usual dipole effect.

Optical Dielectric Constant and Atom Polarization

The optical dielectric constant ε_∞ is often assumed as equal to the square of refractive index for visible light. But the refraction of visible light is due primarily to the displacement of electrons, while ε_∞ is due to the displacement of both electrons and atoms in the molecule. The small difference between the two determines the magnitude of the atom polarizations. Regarding the latter quantity there exists no general relationship, but sometimes it was assumed for the sake of convenience that the atom polarization amounts to 5% or 10% of the electron polarization[14].

There is available no literature concerning the refractive index of Japanese coals. The only existing data are those on European coals by van Krevelen[4] who found a relation between the refractive index and carbon content (see curve 3 in Fig. 4).

Dielectric constant of Mayazi coal B (C% 85.24) measured at a micro-wave frequency (4000 Mc/s) is 3.35[15]. This ε value is just equal to the square of the same carbon content estimated from the curve (n_D=1.83). From this astonishing coincidence, one may imagine that ε at the frequency of 4000 Mc/s is equal to ε_∞, and further that the contribution from atom polarization is insignificant. Yatake coal (C% 89.4) has ε 3.45 at 10 Mc/s which is even smaller than n_D^2=3.65. Again this may indicate that the contribution from the atom polarization is not important.

14) C. P. Smyth, *op. cit.*, p. 416; J. W. Smith. *op. cit.*, p. 256.

15) K. Higasi, I. Miyasita and Y. Ozawa, This Bulletin, **30**, 546 (1957).

By reason of the above it will be assumed in the next section that the square of refractive index for D-line approximately represents ε_∞ of the coal of the corresponding carbon content.

There are two points to be considered against this assumption. First, the neglect of atom polarization is not justified by the above argument. To provide an answer for this, two curves 1 and 2 in Fig. 4 are

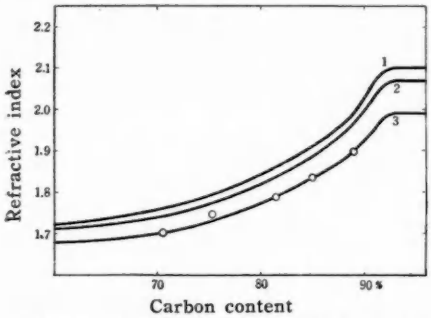

Fig. 4. Variation of refractive index with carbon content. Curve 1, given by the assumption $P_A=7\%$ P_E; curve 2, given by the assumption $P_A=5\%$ P_E and curve 3, observed by van Krevelen[4] on European coals.

plotted. As in usual treatments of atom polarization the following equation is considered.

$$\frac{n'^2-1}{n'^2+2}=(1+\delta)\frac{n^2-1}{n^2+2} \qquad (8)$$

The values of modified refractive indices n' which have been obtained from Eq. (8) are plotted in the graph*. (Curve 2: n' for $\delta=0.05$; curve 1: n' for $\delta=0.07$). By using the values n'^2 for ε_∞, check on the effect of atom polarization will be made.

Second, there is no reason why carbon content should be the determining factor of the refractive index. Further, one is not certain whether or not van Krevelen's relation obtained for European coals is applicable to all the Japanese coals. Under these circumstances any discussion on ε_∞ has ambiguity to be cleared up in the future.

* The choice of $\delta=0.05$ for the correction of the atom polarization is a practice due to Groves et al. (*J. Chem. Soc.*, 971 (1935); 1779 (1937)). The reason for choosing $\delta=0.07$ is as follows. Suppose that coal is composed of two parts: for the major part (70 %), P_A is taken as 3.4 % P_E from the data of benzene, toluene and ethylene, and for the remaining part (30 %), $P_A=15\%$ P_E is assumed from the data for alcohols, ethers and ketones (J. W. Smith, op. cit., Table 39, p. 261). Atom polarization of coal will then have the value of 7 % of P_E, viz., $\delta=0.07$.

Molecular Volume and Dipole moment

Difficulties in measuring the molecular weight of coal are well-known. It is not right to speak of a molecual dipole moment for a substance with unknown molecular weight. But this situation may be saved by considering the fact that a molecular dipole in coal may not rotate as a whole. Actually some rotatable groups in a molecular unit will orient with the direction of an externally applied field. Therefore the "molecular weight" for the present study need not to be a definite quantity.

In the present work a molecular volume 300 cc will be somewhat arbitrarily chosen without regard to the actual weight of coal. Dipole moments of coals are all to be calculated with reference to this volume. If the density of the coal is 1.4, the apparent molecular weight will amount to 420. Dipole moments thus calculated from Eq. (2) are summarized in Tables I and II. Values in Table II are obtained

TABLE I

DIPOLE MOMENTS OF COALS

	Coal	C %	ε/freq.	ε_∞	μ
VI	Tempoku (brown coal)	66.62	5.56/1 kc (5.20/1 Mc)	2.87	1.78 (1.69)
Vb	Mitui-bibai	78.40	4.19/1 Mc	3.07	1.24
Va	,,	80.12	4.10/1 Mc	3.14	1.15
V	,,	80.47	3.61/1 Mc	3.15	0.83
Vc	,,	80.62	(4.70/1 kc)	3.16	(1.39)
IV	Akabira	80.76	3.66/1 Mc	3.16	0.86
II	Moziri	81.71	3.92/1 Mc (4.37/1 kc)	3.20	1.01 (1.23)
IIIa	,,	82.07	3.69/1 Mc	3.21	0.84
III	,,	82.98	3.88/1 Mc	3.26	0.93
I	,,	85.25	4.47/1 Mc	3.35	1.18

Values without parentheses are preferred.

TABLE II

DIPOLE MOMENTS OF COALS

(ε is estimated from powdered mixture)

	Coal	C %	ε/freq.	ε_∞	μ
E1	Taihei (lignite)	65.1	4.78/1 kc (4.45/1 Mc)	2.86	1.58 (1.48)
E2	Tempoku (brown coal)	70.2	4.58/1 kc (4.38/1 Mc)	2.90	1.50 (1.43)
C7	Sunagawa	81.84	3.98/1 Mc	3.20	1.04
C3	,,	82.09	3.56/1 Mc	3.21	0.72
B	Mayazi	85.24	4.02/1 Mc	3.35	0.95
F4	Pocahontas (U.S.A.)	87.99	4.83/10 Mc (5.16/1 Mc)	3.53	1.22 (1.33)
F1	India	88.03	4.71/10 Mc (5.00/1 Mc)	3.54	1.17 (1.27)
F5	Durham (England)	89.31	5.18/10 Mc (5.51/1 Mc)	3.63	1.29 (1.39)
D1	Yatake	89.4	3.45/1 Mc	3.65	0

from powdered mixtures, so that they are less accurate*.

Groenewege, Schuyer and van Krevelen[16] gave a dipole moment 0.5 D for a certain coal. No particulars were reported except that they employed Eq. (2) and that the molecular weight for the coal was taken as 420.

Discussion

Polar groups which might exist in coals[17] will be assumed to have the following magnitudes of dipole moments. O-H 1.51; C-O 0.74; C=O 2.3; N-H 1.31 D[18]. Some of these groups must interact upon each other**, and some others must be in a state of complete non-rotation on account of the strong field of lattice forces. Suppose as an extreme case in spite of the above, that all these groups can rotate independently. Then the resultant moment μ will be given by

$$\mu^2 = 1.51^2 n_{O-H} + 0.74^2 n_{C-O} + 2.3^2 n_{C=O} + 1.31^2 n_{N-H} \quad (9)$$

where n_{O-H}, n_{C-O}, etc. represent the number of O—H groups, etc. in a molecule —or more exactly in a molecular unit defined by $M/d=300$. In a special case in which none of the others except the O—H group are important so that they can be neglected,

$$n_{OH} = \mu^2/2.28 \quad (10)$$

The numbers of O—H groups will then be calculated. The polarity of brown coals corresponds approximately to one rotatable O—H group, while others to some small fractions in the molecular unit.

For three specimens of Moziri coals a comparison is made between calculated values and the results of chemical analyses.

TABLE III

A COMPARISON WITH CHEMICAL COMPOSITION

	Coal	C %	O %	d	M	N_{oxy}	n_{O-H}
I	Moziri No. 4	85.25	6.91	1.357	407	7.00	0.61
II	,, No. 3	81.71	9.78	1.340	402	8.04	0.45
III	,, No. 9	82.98	9.07	1.304	391	7.39	0.39

Table III shows the values of the molecular weights as calculated from specific gravities and $M/d=300$. From M and C%, the number of oxygen atoms, N_{oxy}, in this molecular unit is obtained. The ratio n_{O-H}/N_{oxy} is 0.05–0.09. Reliablility of such estimation is certainly low, but it suggests that the rotatable part is only a small fraction of the total oxygen.

It is evident from Table II that Yatake coal (D1) is non-polar. Besides the fact that no moment is detected, there is also no anomalous dispersion in the wide range of frequencies. (See curves in Figs. 3 and 4 in the preceding paper[3].)

For some coals (IIIa, IV and C3) small moments below 0.9D are observed. Regarding these small moments there is uncertainty whether they are real or not. To make this point clearer a little examination on errors will be necessary. First, error in measuring ε amounts to 5–10 %. If the deviation in ε is 0.2–0.4, a small moment below 0.5–0.7D will not be distinguishable from zero. See curve b in Fig. 1. Second, there exists an error concerning the estimation of atom polarization, even if van Krevelen's relation be actually valid. An inspection of curves in Fig. 4 will reveal that a small moment less than 0.6 D is unreliable. Under these circumstances it may not be wise to enter into any serious discussion on small moments observed.

Besides the comparatively small polarities found for bituminous coals there is another phenomenon which seems to suggest that these coals are nearly non-polar. That is, there has been observed scarcely any distinct dispersion* in the frequency range of this experiment. See curves A for a Moziri coal in Figs. 2 and 3.

There is one important fact in this connection that Mayazi coal, which has a moment value 0.95 D, shows a remarkable change in ε between 4000 Mc/s and 10 Mc/s[15]. This strongly suggests that anomalous dispersion due to dipole rotation exists in this region and therefore that the magnitude 0.9 D is real. This is encouraging, but it may not be very convinicing. In view of the fact that the above offers just one example and further that the microwave measurement of the desired accuracy is still lacking, it is premature to speak, with confidence at least, of the polarity of these bituminous coals.

* Maximum errors in ε are ± 5 % in Table I and ± 10 % in Table II.

16) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

17) See for instance, R. A. Friedel and J. A. Queiser, *Anal. Chem.*, **28**, 22 (1956).

18) C. P. Smyth, *op. cit.*, p. 244.

** Regarding the interaction between polar groups see for example S. Mizushima, Y. Morino und K. Higasi, *Physik. Z.*, **35**, 905 (1934); S. Mizushima, "Structure of Molecures and Internal Rotation," Academic Press, New York (1954), p. 7.

* Excepting those in the low frequency region which may be due to other causes.

Summary

If coal be regarded as a supercooled liquid, a basis will be provided for determining the dipole moment of coals. Further uncertainty as to choosing a proper equation for liquids is dispelled by the fact that the Onsager equation gives for coal almost the same magnitude of dipole moment as obtained by the Debye equation.

After discussion focussed on the values of the ordinary and optical dielectric constants, dipole moments are evaluated for 19 coal specimens including four samples of foreign origin.

Brown coals are found to have a moment near to that of one O—H group. The polarity of bituminous coal is in general too small to be distinguishable from zero. These results are consistent with the observations on the frequency dependence of dielectric constant and loss factor of these coals.

Thanks are expressed to Drs. Y. Ozawa and M. Kugo for valuable discussion.

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SHORT COMMUNICATIONS

On the Anion-Exchange Behavior of Some Quadrivalent Actinide Elements

By Nobufusa SAITO and Tatsuya SEKINE

(Received April 5, 1957)

It has been well established that thorium (IV) is not adsorbed on an anion exchange resin from hydrochloric acid solution of any concentration. This fact makes it possible to separate thorium(IV) cleanly from any elements which do form negative ions adsorbable on an anion resin[1]. In 1953, Jenkins and Richardson studied the uptake of thorium(IV) on an anion exchange resin such as Deacidite FF, from solutions containing nitrate and sulfate[2].

The present authors are continuing a systematic study on the adsorbability of quadrivalent actinide elements on anion-exchange resins. It has been observed that thorium(IV) is adsorbed on Dowex 1 both from sulfate and carbonate solutions, while neptunium(IV) is adsorbed from carbonate solutions. The good uptake of uranium(IV) on that resin from a sulfate solution was also observed.

Dowex 1-X8 of 100–200 mesh was employed in this experiment. In column studies, resin columns of 5.0 cm. $\times$ 0.5 cm^2 were used. In equilibrium studies, Dowex 1 of sulfate form was first dried for three hours at 70°C and kept in a desiccator over a saturated solution of sodium bromide. The tracer solutions employed were thorium-234 in concentrated nitric acid and neptunium-239 in 6 N hydrochloric acid containing sulfur dioxide. The thorium(IV) solution was almost evaporated to dryness on a water bath and the residue was dissolved in solutions of ammonium sulfate or sodium carbonate of various concentrations. The neptunium (IV) solution was prepared by dissolving the residue in sodium carbonate solution containing a small amount of sulfur dioxide.

The radioactivity of the tracer was measured with a thin end-window Geiger-Müller tube after the tracer was coprecipitated with 5 mg. of ferric iron from acidified sample solutions with ferric hydroxide. In the case of samples containing thorium-234, the radioactive equilibrium between thorium-234 and protactinium-234 was attained at the time of measurement.

a) Experiments on thorium(IV) and uranium(IV) in solutions.

1) E. K. Hyde, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol, 7, 281 (1956).
2) I. L. Jenkins and R. J. Richardson, A.E.R.E. C/R 1217. (1953).

i) Column studies.

After a resin bed of sulfate form was thoroughly washed with 0.1 M ammonium sulfate solution, 5 ml. of thorium(IV) solution was placed on the top of the column, and allowed to flow down through the column at a rate of 0.3–0.5 ml. per min.. The adsorption of thorium(IV) from 0.1 M ammonium sulfate solution was so complete that no activity of thorium-234 was detected in the effluent. The adsorbed thorium(IV) was easily eluted with 1 N hydrochloric acid solution. The elution curve is shown in Fig. 1.

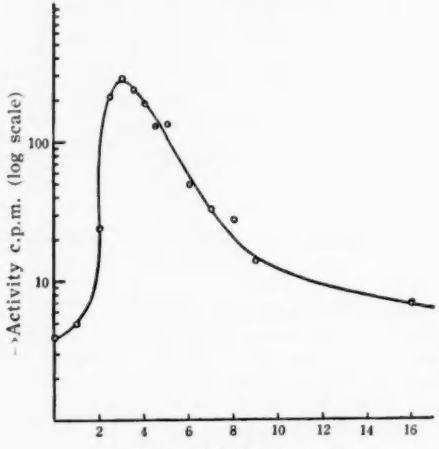

Fig. 1. The elution curve of Th(IV) with 1 N HCl. Column 5cm. × 0.5cm² Dowex 1-X8 100–200 mesh.

Quadrivalent uranium, in macro quantities, was adsorbed on a resin bed of sulfate solution containing zinc, which was used for the reduction of uranyl ions. A green adsorption band appeared near the top of the bed. Washing of the column with 10 ml. of 0.01 M ammonium sulfate solution brought about no appreciable shift of the band. The adsorbed uranium (IV) was easily eluted with 6 N hydrochloric acid.

ii) Equilibrium studies.

Some experiments were carried out on thorium(IV). A weighed portion of the resin was allowed to stand overnight in a solution of ammonium sulfate under consideration. After the resin and the solution were placed in a glass-stoppered Erlenmeyer flask, the whole was shaken on a mechanical shaker in a thermostat at 25°C, until the exchange equilibrium was attained. In this case, a certain amount of thorium-232 was added to the tracer solution so that the equililbrium was reached at 0.1–1% loading of thorium (IV) with respect to the resin capacity. The following values of the equilibrium distribution coefficient, K_d (activity per g. of resin/activity per ml. of solution) were obtained: at 25°C, K_d=21 for the adsorption of thorium(IV) from 1 M ammonium sulfate solution, K_d=310 from 0.01 M ammonium sulfate solution.

b) Experiments on thorium(IV) and neptunium(IV) in carbonate solutions.

Only column studies were carried out. Thorium(IV) was adsorbed on a resin bed from 0.1 M sodium carbonate solution. No activity of thorium-234 was detected in the effluent. A part of adsorbed thorium (IV) was eluted with 10 ml. of 4 M ammonium chloride. Then most part of thorium(IV) was removed with 20 ml. of 6 N hycrochloric acid solution. A similar adsorption of neptunium(IV) from 0.1 M sodium carbonate solution was observed in preliminary experiments. The nature of adsorption of these elements from carbonate solution is not clear as yet.

Details of the present study will be published elsewhere in the near future.

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